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ISOTOPIC STUDIES OF RETARDATION
OF EVAPORATION OF WATER BY CETYL
ALCOHOL FILMS

by



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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled ISOTOPIC STUDIES OF RETARDATION OF EVAPORATION OF WATER BY CETYL ALCOHOL FILMS, submitted by Adel Ahmed Bakr in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

In order to elucidate the role of cetyl alcohol films in retarding the evaporation of water, $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ abundance ratios were determined during evaporation of water without films and with films of various thicknesses.

It was found that the isotopic fractionation with films is slightly larger than without films. Increasing the film thickness appears to promote a greater isotopic selectivity. However, the effect is not appreciable and it is concluded that cetyl alcohol films do not introduce an isotopically selective step which can effectively compete for rate control in the evaporation process.

The isotope techniques show some promise for elucidating the mechanism of evaporation retardation by films. However, the experiments to date suggest that careful attention must be given to problems such as container design and the control of temperature and humidity.

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CHAPTER 1

EFFECTS OF FILMS ON THE RETARDATION OF EVAPORATION OF WATER

1.1 Monolayers

It has been known for many years that monolayers of a number of long chain compounds or layers of appropriate oil mixtures on water surfaces may retard evaporation (ADAM, 1925; RIDEAL, 1925; DOCKING et al., 1940; SEBBA and BRISCOE, 1940; POWELL, 1943; GILBY and HEYMANN, 1948).

The use of monolayers for evaporation reduction holds considerable promise for water conservation. An estimated 11.5 million acre-ft of water are lost each year by evaporation from large lakes and reservoirs in the western United States (TIMBLIN et al., 1962).

A monolayer has to fulfill two conditions: Firstly, it has to be compact with strong cohesion forces between the paraffinic residual chains. Secondly, its spreading rate and resealing ability must be good. The first condition assures an effective barrier against evaporation, while the second property maintains the monolayer on the surface despite external disturbances such as wind and wave action. Field work has shown that it is possible to apply and maintain a monolayer on a large reservoir and thereby effectively decrease evaporation. The most commonly used material is cetyl alcohol $[\text{CH}_3(\text{CH}_2)_{15}\text{OH}]$. However, for pure cetyl

alcohol, sublimation loss is significant. This loss may be diminished by using mixtures of cetyl and stearyl alcohol $[\text{CH}_3(\text{CH}_2)_{17}\text{OH}]$, as the latter has a much lower vapour pressure (MANSFIELD, 1962).

Continuous monolayers have been applied to water surfaces by a variety of methods. Most frequently, finely ground dry cetyl alcohol powder is released from a boat (VINES, 1960). Alternately, melted alcohols are sprayed on the surface as a slurry (TIMBLIN et al., 1962). Attempts to use hexadecanol flakes in floating wire cages or so-called rafts proved to be ineffective (MANSFIELD, 1955; TIMBLIN et al., 1962). Depending upon prevailing field conditions, the use of monolayers reduced evaporation losses from 10 to 50% (VINES, 1962).

Numerous laboratory experiments were conducted prior to field work to study the effect of monolayers on the rate of evaporation of water. HEDESTRAND (1924), one of the first investigators, studied the effect of a fatty acid film on the rate of evaporation from a water surface of area 18.2 cm^2 into a current of streaming air at a temperature of 20°C . He concluded that monolayers did not affect the evaporation rate. However, in his experiments, a stagnant layer of air and vapour existed very close to the water surface. He failed to observe any retarding effect for the monolayer because the diffusional resistance of the stagnant air layer was overwhelmingly the rate controlling step in the evaporation.

RIDEAL (1925) was the first to show that monolayers have a marked influence on the evaporation rate of water. He used an inverted U-tube to measure the effect. One arm contained the water at room temperature upon which the monolayer was formed. The other arm was cooled in an ice bath, and the system was evacuated to remove the air column above both water levels. He was able to determine qualitatively the effect of the film on the rate of evaporation by comparing the rates of condensation in the cold arm with and without a surface film on the water. He found that stearic acid $[\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}]$ monolayers reduced the rate of condensation in the cold arm by about 28%. Retardation of evaporation of up to 42% was obtained using other materials.

LANGMUIR and LANGMUIR (1927) also reported that films of cetyl alcohol had a large effect on the rate of the evaporation of water. They tried to determine whether the decrease in the rate of evaporation is due to the stopping of convection currents or impermeability of the film. They concluded that the stopping of surface currents was responsible for the decrease in the evaporation rate. They found that even at atmospheric pressure and winds of about 180 cm/sec, the rate of the evaporation of water was decreased to about one-half by a film of cetyl alcohol. Under similar conditions, fatty acids produced no measurable effect.

To establish the effect of surface pressure on the decrease in the rate of evaporation caused by monolayers,

SEBBA and BRISCOE (1940) passed a stream of dry air inwards from the edge of a metal disc 0.3 cm above the surface of water in a tray provided with barriers and a surface balance. They determined the relative rates of evaporation with and without films and with films exposed to different surface pressures by withdrawing air from a tube at the center of the disk at the rate of two liters per minute and measuring the water content of this air. They found that even compressed films of oleic acid $[\text{CH}_3(\text{CH}_2)_7\text{CH} : \text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}]$ and cholesterol $[\text{C}_{27}\text{H}_{46}\text{O}]$ did not retard evaporation. On the other hand, with arachidic alcohol $[\text{CH}_3(\text{CH}_2)_{19}\text{OH}]$, large effects were obtained. They concluded that the relative decrease in the rate of evaporation was strongly dependent on the surface pressure of the film.

In a subsequent paper, SEBBA and BRISCOE (1940 a) reported that the great decrease in evaporation produced by arachidic alcohol disappeared in a few hours when the film was allowed to remain on the surface under low pressures. This effect did not occur if the film was maintained under high pressure.

LANGMUIR and SCHAEFER (1943) introduced an improved technique for measuring the absolute rate of evaporation through films. This consisted of suspending a porous-bottomed box of a solid desiccant just above the water surface. The amount of water evaporated by a stream of dry air blown over the surface film was measured. The

resistance to evaporation was represented as an energy barrier related to the film pressure. Their results, for various long chain acids, showed very great reductions in the evaporation rate and the effect increased with increasing film pressure. They concluded that two factors determined the rate of evaporation: (1) There must be a decrease in the partial pressure of water vapour as it diffuses through the air overlying the liquid; (2) The effect of a film of cetyl alcohol is to offer a resistance to diffusion which resides in the monolayer itself.

ARCHER and LA MER (1954) made measurements in the trough of a surface balance, so that the resistance to evaporation can be determined as a function of the film pressure and molecular area of the monolayer. The technique used is a development of the method employed by LANGMUIR and SCHAEFER described earlier. They used anhydrous lithium chloride as the desiccant since it produces a greater rate of absorption and exhibits less caking and less adherence to the membrane over which it is suspended. They reported that the transport of water from the water surface to the desiccant surface involves evaporation from the water surface, diffusion through the separating air column and the membrane followed by condensation or absorption at the desiccant surface. They described the above processes mathematically and derived the diffusion coefficients and some other parameters involved. ARCHER and LA MER (1954) studied the

resistances of compressed fatty acid monolayers as a function of the chain length, subphase composition, state of the monolayer and temperature. They found that the resistance depends markedly on the chain length of the molecule but is independent of pressure in the range measured.

ROSANO and LA MER (1956) carried out extensive studies comparing the behaviour of the fatty acid monolayers with that of esters, acids, and alcohols. They found that monolayers of esters usually exhibit a negligible effect on evaporation. Alcohols were found to exhibit no specific resistance over a wide range. The specific resistance of alcohols rises continuously with increasing lateral compressing.

LA MER and his coworkers found that if their monolayers were spread using a solution of petroleum ether (a very poor solvent for water) rather than in benzene (which can dissolve some water), and if the spreading was carried out so as to give a highly compressed film directly, then very high film resistances were obtained. Comparing their results with those of LANGMUIR and SCHAEFER (1943), it is found that fatty acid monolayers gave high resistances independent of the film pressure.

The general explanation for the discrepancies between this work and the earlier results seems to be that when films are spread at low pressures with benzene as the solvent, small amounts of water were trapped in the film and

these provided low resistance channels for evaporation. Also, traces of surface active impurities present before spreading may have important effects (ADAMSON, 1964).

1.2 Theoretical considerations of evaporation retardation by monolayers

The concept of an activation energy barrier to the evaporation of water through monolayers was first suggested by LANGMUIR and LANGMUIR (1927) and developed further by LANGMUIR and SCHAEFER (1943). Refinement of this theory in application to the saturated fatty acid monolayers was made by ARCHER and LA MER (1954; 1955). They determined the magnitude of the activation energy for the penetration of the monolayer and its individual CH_2 groups from the temperature coefficient of water transport through the monolayer. The magnitude of this barrier is determined by the energy required by a condensing or evaporating water molecule to penetrate the monolayer.

ARCHER and LA MER (1954) assumed that, over limited areas, the molecules in a monolayer are in a two-dimensional close-packed hexagonal array and that a water molecule in penetrating the film must form a hole in the monolayer equivalent to the area occupied by one film molecule.

They considered a small area of the hexagonal array of molecules. In the initial state, all sites are occupied. After the hole is formed there is one free site in the small

area. However, the mechanism of displacement is such that the total number of molecules in the area is unchanged. Consequently, the intermolecular separation has been decreased, but for a sufficiently large area this change is negligible. If w_{pq} is the potential energy of interaction of a film molecule p with one of its neighbours q , the total interaction energy is the summation

$$\sum_p \sum_q w_{pq}$$

over all of the molecules in the area. In the final state, the total interaction energy is the above summation from which is subtracted the interaction between all of the molecules in the area and the molecule formerly occupying the free site, which is

$$\sum_q \sum_p w_{pq} - \sum_p w_{ap} \quad .$$

Consequently, the energy change is just the interaction between one molecule and all of its neighbours in the monolayer, and is given by

$$W = \sum_p w_{ap} \quad . \quad (1)$$

In the past, various workers (LANGMUIR and SCHAEFER, 1943; ARCHER and LA MER, 1954; 1955) have described evaporation retardation in terms of a "specific resistance to

evaporation", r , offered by the monolayer. They suggest an Ohm's law analogy between this resistance and the specific electrical resistance of a metal in the form

$$r = \frac{F/A}{v} = \frac{\Delta N/A}{v}$$

where

F = the driving force = ΔN ;

ΔN = the difference in concentration between the water vapours in equilibrium with the water below the film and the air above the film respectively;

A = the area of the film;

v = the rate of evaporation.

ARCHER and LA MER (1954) expressed r as

$$r = \frac{1}{\beta u}$$

where β is the fraction of water molecules which penetrates the film with an average velocity u . They then expressed β and u using the Boltzmann equation:

$$\beta = e^{-E/kT} \quad ; \quad \text{and}$$

$$u = \left(\frac{kT}{2\pi m} \right)^{1/2}$$

where

E = the energy barrier to evaporation, the magnitude of which is equal to W in equation (1);

k = the Boltzmann constant;

T = the absolute temperature of the water surface;

m = the mass of the water molecule.

Inserting these values in the above expression for r we get

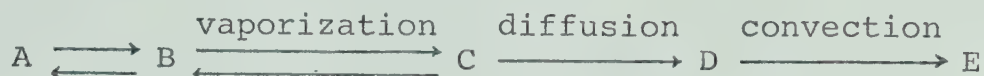
$$r = \left(\frac{2\pi m}{kT} \right)^{\frac{1}{2}} e^{E/kT} \quad (2)$$

This shows that r is proportional to the square root of the mass of the water molecule.

However, MacRITCHIE (1969) argues that the specific evaporation resistance which has often been calculated for monolayers is not a material property as, for example, the specific electrical resistance of a metal. He then pointed out that this analogy breaks down in the case of a reaction sequence involving one or more equilibrium steps, as occurs in mass transport across interfaces and through membranes. He even doubted the validity of the calculation of resistances for different steps from kinetic data.

MacRITCHIE (1968) tested the hypothesis that cetyl alcohol acts by influencing the thickness of the stagnant fluid layer next to the interface by measuring the temperature gradient near the surface. He found that hexadecanol (cetyl alcohol) has no effect on the evaporation rate when the latter is controlled by a thick diffusion layer. The percentage retardation of evaporation by hexadecanol increases markedly with increasing velocity of air circulation. He concluded that a hexadecanol monolayer acts by resisting the reduction of the stagnant layer thickness by air currents.

In discussions of the role of the monolayer, it is useful to consider the sequence of steps in the evaporation process as follows:



where, $A \rightleftharpoons B$ represents the equilibrium between liquid molecules in the bulk and in the surface. One would expect that the establishment of this equilibrium is very rapid. This equilibrium is not considered to be influenced by the presence of a monolayer, since this would lead to changes in the surface tension, which have not been observed by MacRITCHIE (1969). The expression $C \rightarrow D$ represents the molecular diffusion of vapour through a diffusion boundary layer. The evaporation rate v is generally equal to the rate of this diffusion step and could be described by the equation:

$$v = \frac{D(C_0 - C)}{x} \quad (3)$$

where D is the diffusion coefficient, x is the effective thickness of diffusion layer, and C_0 and C are concentrations at the two surfaces of the diffusion layer. It has been concluded (MacRITCHIE, 1968) from measurements of the temperature gradient near an evaporating surface that monolayers of hexadecanol influence the magnitude of x . However, it cannot be concluded with certainty that this is the only role of the monolayer in evaporation reduction (MacRITCHIE, 1969). This

is due to the difficulty in measuring temperature gradients precisely and to the fact that the diffusion and thermal boundary layers need not always be identical.

According to MacRITCHIE (1969), monolayers influence the evaporation by means of an artificial barrier which retards the vaporization step $B \rightarrow C$ in the equilibrium $B \rightleftharpoons C$ established between water molecules in the surface and an adjacent layer of vapour molecules. However, experiments carried out by POWELL (1943) showed that multimolecular films ($\sim 1 \mu$ thick) are required to provide a significant barrier for diffusion of molecules from the liquid to the vapour. If a monolayer were to retard step $B \rightarrow C$, then the rate of evaporation in the steady rate could still be described by equation (3), except that C_0 would now have a value below the equilibrium vapour concentration. The retarding effect of the monolayer in this hypothetical case would then depend on the rate of step $C \rightarrow D$ and would vary according to the conditions, becoming zero when step $C \rightarrow D$ is made sufficiently slow.

To determine which step a monolayer affects when it retards the evaporation rate, a simple test may be carried out. In case of water, the amount of retardation caused by the monolayer is measured under several different conditions of forced convection at one value of the ambient relative humidity. The series of experiments is repeated at another value of the relative humidity, sufficiently different to

alter the absolute rates appreciably. If the monolayer alters the evaporation rate by affecting the vaporization step only, then the percentage of retardation should depend on the absolute rate of evaporation and not on the conditions. Whereas if it affects the diffusion layer, the retardation should depend on the hydrodynamic conditions and be independent of the absolute rate. An intermediate result would be expected if both mechanisms operate.

MacRITCHIE (1969) carried out several experiments along the lines described above. He concluded that the retardation of evaporation by hexadecanol monolayers is the same under comparable conditions of convection and is independent of the absolute rate of evaporation. He also concluded that the hexadecanol monolayer produces no barrier to the vaporization step and exerts its effect by altering the hydrodynamic boundary conditions.

When air is passed over a liquid surface, there is always some movement of the surface as a result of the net stress due to the air. If a sufficiently incompressible monolayer is placed on the surface, the stress τ due to the moving air compresses the monolayer. This produces a surface pressure gradient $d\pi/dx$ which opposes the stress. The back stress of the monolayer reduces the net stress on the surface and therefore consequently increases the size of the boundary layer.

MacRITCHIE (1969) carried out experiments assuming laminar flow with the highest air velocity U_0 as 480 cm/sec. If no net flow of the monolayer occurs under steady state conditions, then

$$\tau = \frac{d\pi}{dx}$$

where τ is the stress due to the moving air and $d\pi/dx$ is the surface-pressure gradient opposing τ . He showed that very small surface pressure gradients can cause significant changes in boundary layer properties and consequently evaporation rates. He then concluded that the reduction in the steady state rate of evaporation of water by hexadecanol monolayers depends only on the air velocity above the surface. The reduction is found to be independent of the absolute rate of evaporation up to air velocities of 40 cm/sec. This indicates that the monolayer does not affect the vaporization step but increases the size of the diffusion boundary layer.

KAPPESSER et. al. (1969) reexamined MacRITCHIE's experiments and found that his data are consistent with those obtained for turbulent flow. They argue that he did not have a laminar flow system since a fan was used which may introduce a complicated rotational motion, with vortices starting from the ends of the blades.

MacRITCHIE (1969) showed that the evaporation retardation ratio v_w/v_0 is independent of the relative humidity at a given Reynolds number where v_w and v_0 are the evaporation

rates with and without hexadecanol respectively. He then concluded that the hexadecanol produces no barrier to the vaporization step but exerts its effect by altering the hydrodynamic boundary layer. However, KAPPESSER et al. (1969) found that the presence of a vaporization step with hexadecanol also yields results which are consistent with the above experimental observation.

1.3 Multimolecular layers

HEYMANN and YOFFE (1942) carried out experiments on the stability of multimolecular films of hydrocarbon oils, containing spreaders, on water surfaces. The layers were spread on water in Petri dishes, filled to a constant distance from the top of the dish. Petroleum ether was sometimes used as solvent in putting on the oil and it evaporated quickly. Evaporation tests were conducted over a period of one day in a large chamber shielded from draughts and sunlight. The temperature and humidity were recorded. The reduction in the rate of evaporation was determined by comparing the loss of weight, per sq.cm. of surface, from the oil covered and from a clean water surface under the same conditions. They found that the multimolecular layers retard the evaporation sufficiently to be of practical value. They showed that films of polymerised oil of considerable stability can be obtained. These films reduce the evaporation into still air by 58 to 78% when the thickness is 5×10^{-4} cm and 70 to 81% when the thickness is 10×10^{-4} cm.

POWELL (1943) conducted a series of experiments on the influence of surface films of oil of thicknesses ranging to about 2.5 cm on the evaporation of water. The rate of loss of weight was determined from surfaces contained in straight-sided glass dishes about 4 cm deep and 6.8 cm in diameter filled within about 0.4 cm of the brim. POWELL found that there is an optimum thickness for a given oil film for which the rate of evaporation from the underlying water surface has a minimum value. He concluded that the retardation of evaporation with multimolecular films of oil was appreciably greater than with monomolecular films. He also reported that the effectiveness of the films becomes relatively greater as the air velocity is increased, and that the order of the effect can be estimated from a knowledge of the diffusion coefficients of water vapour through air and oil.

1.4 Isotopic fractionation and the possible elucidation of evaporation retardation mechanisms

In view of the controversies which have arisen in describing the role that surface films play in retarding evaporation, we decided to examine alterations to $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ and $\text{HDO}/\text{H}_2\text{O}$ abundance ratios during evaporation. If the concept of a "specific resistance to evaporation", as given by LANGMUIR and SCHAEFER (1943) and ARCHER and LA MER (1954), is reasonable, equation (2) states that this quantity is

proportional to the square root of the mass of the water molecule. By measuring the isotopic effects occurring with and without surface films, it can be ascertained whether the film indeed introduces an isotopically dependent step into the process and hopefully some of the controversy can be resolved. Accordingly, the next chapter is devoted to a review of the fractionation of isotopic species of water during evaporation.

CHAPTER 2

FRACTIONATION OF ISOTOPIC SPECIES

OF WATER DURING EVAPORATION

2.1 Introduction

The abundances of the most important isotopic components of water, H_2O^{16} , HDO^{16} , and H_2O^{18} , are approximately 99.768:0.032:0.200 %, depending on the origin of the water (DANSGAARD, 1964).

Isotopic abundances of water species are usually determined mass spectrometrically. Since isotopic compositions can be compared with better precision than the accuracy with which absolute abundances can be measured, isotopic variations are expressed on δ scales in ‰ as follows:

$$\delta\text{D in } \text{‰} = \left[\frac{[\text{D/H}]_{\text{sample}}}{[\text{D/H}]_{\text{standard}}} - 1 \right] \cdot 10^3$$

or

$$\delta\text{O}^{18} \text{ in } \text{‰} = \left[\frac{[\text{O}^{18}/\text{O}^{16}]_{\text{sample}}}{[\text{O}^{18}/\text{O}^{16}]_{\text{standard}}} - 1 \right] \cdot 10^3 \quad (4)$$

The standard used by most laboratories for both δD and δO^{18} values of water is SMOW (standard mean ocean water, CRAIG, 1961 a).

Isotopic fractionation of water can be effected by several processes such as biological activity and isotopic exchange with other materials. However, the fundamental

reason for the significant terrestrial variations in the heavy isotope content of natural waters is that the vapour pressure of H_2O^{16} is higher than those of HDO and H_2O^{18} . This leads to variation in the relative amounts of these isotopic species of water in precipitation. The temperature and the rate of reaction affect the fractionation factors for the various processes mentioned above.

2.2 Isotopic equilibrium exchange processes

We shall discuss only two-phase systems with no supply of material from the environment. When a process proceeds slowly so that equilibrium conditions are attained at the boundary between the phases, the fractionation factor α for evaporation of liquid water becomes the ratio

$$\alpha = \frac{p_1}{p_2}$$

where p_1 , and p_2 are the vapour pressures of the light and the heavy components respectively.

At room temperature, the fractionation factors for HDO and H_2O^{18} are 1.08 and 1.009, respectively. This means that vapour in equilibrium with water is depleted some 80 ‰ in deuterium and 9 ‰ in O^{18} relative to the water (REISENFELD and CHANG, 1936; MERLIVAT et al., 1963). MERLIVAT et al. (1963) measured the fractionation factors for deuterium and O^{18} at temperatures $>0^\circ\text{C}$. They also obtained α_{18} at temperatures extending to -20°C using

ZHAVOROWKOV's formula (DANSGAARD, 1964);

$$\alpha_{18} = 0.9822 \exp(15.788/RT)$$

where R is the gas constant.

Slow evaporation with the immediate removal of vapour from the remaining water is known as a Rayleigh process. Such processes lead to higher fractionation than in processes, in which the two phases are allowed to equilibrate by exchange. Evaporation under the latter conditions probably seldom occurs in nature. DANSGAARD (1964) used the formula:

$$\delta_{\omega} = F_{\omega}^{\epsilon} - 1 \quad ; \quad \epsilon = \frac{1}{\alpha} - 1$$

to obtain the δD and δO^{18} for a water reservoir evaporating under Rayleigh conditions. In this formula δ_{ω} is the composition of the remaining fraction F_{ω} of the water reservoir, if the initial composition is assumed to be $\delta_{\omega}^O = 0$. The calculated δD and δO^{18} for $F_{\omega} = 0.3$ and 0.1 at various temperatures are listed in Table 1. It is to be noted that all the δ 's are positive due to the preferential escape of H_2O^{16} .

2.3 Non-equilibrium (fast evaporation) processes

Here the situation is complicated by the existence of kinetic isotope effects during the change of phase. Although the detailed mechanism is unknown, we can interpret the results by assuming that the rate of reaction, K,

Table 1

δO^{18} and δD of the remaining fraction of
a water reservoir undergoing isothermal
evaporation (after DANSGAARD, 1964)

$F_{\omega} = 0.3$			$F_{\omega} = 0.1 \rightarrow 1$	
$t^{\circ}C$	$\delta D \text{ }^{\circ}/\text{oo}$	$\delta O^{18} \text{ }^{\circ}/\text{oo}$	$\delta D \text{ }^{\circ}/\text{oo}$	$\delta O^{18} \text{ }^{\circ}/\text{oo}$
0	122	13.4	247	25.8
20	92	11.1	184	21.5
40	71	8.9	140	17.1
60	54	7.1	107	13.6
80	44	5.4	86	10.0
100	34	4.0	67	7.6

of the light component is the fastest, i.e.

$$K(H_2O^{16}) > K(HDO) > K(H_2O^{18}) .$$

The relatively fast escape of H_2O^{16} during fast evaporation leads to effective fractionation factors α_{eff} , which are higher than the α identified with equilibrium exchange conditions. DANSGAARD (1961) reported values of α_{eff} for O^{18} up to 1.019, corresponding to a 100 ‰ increase of $\alpha_{18} - 1$.

2.4 Terrestrial variations

In nature, indications of significant kinetic isotope effects have been found only in very localized evaporation phenomena (CRAIG et al., 1956; BOATO, 1960; CRAIG, 1961 b; EHHAULT et al., 1963; CRAIG et al., 1963).

Usually evaporation (and precipitation) of natural waters occurs in environments containing water vapour. Therefore, one cannot rule out the possibility of isotopic exchange between the vapour and liquid phases.

The isotopic composition of natural precipitation at any site is determined by numerous factors which are summarized below:

(a) Distance from the source: The vapour leaves the source (usually the ocean) with slightly negative δ values than the source. As the vapour moves away from the source

(inland from oceans), precipitation becomes progressively lighter because of preferential precipitation of the heavier molecules.

(b) Temperature (altitude and latitude effects):

A decrease in temperature increases the isotopic fractionation factor for evaporation. This means that the vapour released at cooler temperatures together with the precipitation derived from it will be more depleted in the heavier isotopic species. It is noted that continental precipitation generally becomes more depleted in the heavier isotopic species with increasing latitude with the greatest depletion occurring at the poles. Precipitation also becomes isotopically lighter with increasing altitude. Both these effects result essentially from the temperature effect with reservoir effects mentioned in (a) also playing a role.

(c) Exchange during precipitation: When precipitation occurs, water droplets are exposed to the humidity of the atmosphere. Exchange can occur between the raindrops and the atmospheric vapour. This effect depends on the drop size, the duration of rainfall, and the temperature. In the case of heavy rains the effect is negligible, since the initial fall of rain sweeps out the prevailing atmospheric vapour and provides a new vapour source (DANSGAARD, 1953; FRIEDMAN et al., 1962; CRAIG et al., 1963; EHHALT et al., 1963).

(d) Evaporation of precipitation: Evaporation is relatively high in dry air, in which case the process probably proceeds under nonequilibrium conditions (EHHALT et al., 1963). On the other hand in the case of high humidity, exchange will be the dominating factor (FRIEDMAN et al., 1962).

DANSGAARD (1964) reported the following relation between δD and δO^{18} for many stations in the Northern Hemisphere:

$$\delta D = (8.1 \pm 0.1) \delta O^{18} + (11 \pm 1) \text{ }^{\circ}/\text{oo} \quad .$$

He interpreted this equation as representing evaporation in a non-equilibrium process from SMOW and precipitation under equilibrium conditions. He also found that relationships exist between the mean annual temperature and the O^{18} and D content in precipitation for a large number of continental stations throughout the world as follows:

$$\delta O^{18} = 0.69 \text{ }^{\circ}\text{C} - 13.6 \text{ }^{\circ}/\text{oo}$$

$$\delta D = 5.6 \text{ }^{\circ}\text{C} - 100 \text{ }^{\circ}/\text{oo} \quad .$$

2.5 Summary relevant to isotopic studies

It would appear that isotopic studies are desirable from two viewpoints.

(1) Isotopic studies may resolve some of the controversial aspects of evaporation retardation by films. For

example, can one utilize the concept of a "specific resistance" which is proportional to the square root of the mass of the diffusing water molecule? If the only effect of the film is the reduction of air currents, then negligible isotope effects should be introduced by the film. Information obtained about the mechanism of retardation should aid in the selection of more effective evaporation retardants.

(2) If films alter the isotopic behaviour of evaporation, this could have some terrestrial implications. (Terrestrial water surfaces are often covered with natural films.)

CHAPTER 3

EXPERIMENTAL

The experimentation was designed to determine the isotopic effects introduced during evaporation of a water surface sprayed with cetyl alcohol films. This was achieved by measuring the $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ ratios of remaining liquid water samples during the course of evaporation. Simultaneous measurements were made on waters with various film thickness and without a film.

Identical rectangular transparent plastic containers of area $24 \times 17 \text{ cm}^2$ were used. The containers were filled initially with water to a depth of about 8 cm and the depth was measured by a scale attached to the outer surface of a wall of the container.

Before filling, the containers were washed thoroughly with "Alconox laboratory detergent" and then rinsed thoroughly with deionized distilled water. In each container, equal volumes of deionized distilled water were placed to evaporate under the selected conditions. Using advice from MacRITCHIE (1969), solutions of cetyl alcohol in heptane (0.05 gm cetyl alcohol in 100 cc heptane) were sprayed over the water surface using a syringe. The heptane subsequently evaporated to leave the cetyl alcohol film.

Samples of about 5 cc of water were taken from each container regularly using a syringe with a fine needle to

avoid breaking the film. After sampling from one container, the syringe was dried before using it to sample another container. The samples were stored in tightly closed vials to prevent evaporation and the associated isotope fractionation.

The experiments were conducted under the following conditions:

(a) Run No. 1

(i) Compressed air dried by passing through a Dry Ice trap, was blown at a rate of 10 liters/sec over the surface of water in containers placed in a wooden box with two identical compartments.

(ii) The water surface of one of the containers was sprayed with 15 cc cetyl alcohol solution.

(b) Runs Nos. 2 and 7

(i) The containers were placed under the fume hood of the clean room.

(ii) In run no. 2 the water surface of one container was sprayed with 10 cc of the organic solution. Three containers were used for run no. 7, two of which were sprayed with 0.2 and 1.0 cc of the solution respectively.

(c) Runs Nos. 3-6

(i) Water in the containers was left to evaporate out in the open in the clean room.

(ii) In runs nos. 3 and 4 the water surface of one container was sprayed with 4.5 and 2.5 cc of the cetyl alcohol solution respectively.

(iii) Four containers were used in run no. 5, three of which were sprayed respectively with 0.1, 0.5 and 1.0 cc of the solution. Due to the sharp rise in room temperature because of the operation of a furnace in the clean room, sampling was not completed. Hence, run no. 6 is a repetition of no. 5.

At the start of each of the above mentioned runs, a reference sample was taken from the same water used to fill the containers. The temperature and the relative humidity (measured by an "Airguide Humidity Indicator", Model 605) were recorded constantly during all but the first run.

The method used in determining the relative O^{18} concentrations of the water samples is described by EPSTEIN and MAYEDA (1953). It consists of isotopically equilibrating a small amount of purified commercial carbon dioxide with water in a thermostated bath and then analyzing the CO_2 gas mass spectrometrically. The pH of the water samples was adjusted to 6 or lower by the addition of a drop of HNO_3 to allow for more rapid equilibrium to be established. 2 cc of water was then added to a bulb which was placed on a vacuum line. The water was frozen using liquid nitrogen and the trapped gases were pumped away. The ice is then melted and warmed to room temperature to release any gas

trapped during the initial freezing. The water is then refrozen using a Dry Ice-acetone bath and then pumped momentarily to remove remaining gases. Commercial carbon dioxide was introduced into each bulb at a pressure slightly below one atmosphere. The bulbs were removed and equilibrated at 25°C for two days. They were shaken frequently over the period of equilibration to ensure that water deficient in O^{18} does not remain condensed on the walls of the vessels. The water level of the bath was always kept just above the stopcock of the bulb to provide uniform temperature throughout the vessel and thus prevent condensation on the interior walls. The carbon dioxide was transferred to breakseals after equilibration. In this operation, the water was frozen with a Dry Ice-acetone bath and CO_2 gas was passed through a trap immersed in a similar bath for thorough H_2O removal.

A magnetic analyzer mass spectrometer which simultaneously collected ion currents corresponding to masses 44 + 45 and 46, was used for the isotopic analysis.

CHAPTER 4

RESULTS

The results are now summarized in the order in which the experiments were performed.

Run No. 1 (Compressed air stream, twin chambers).

The percentage evaporation as a function of time with and without film is shown in Fig. 1. After 36 days, only 26 percent of the water which initially had no surface film evaporated. The rate of evaporation without film was 1.5 times that with film. At this point in the experiment, the accumulation of dust particles on the film and/or the air flow ruptured it. Further, the initially "clean" surface was obviously covered with a layer which was perhaps derived from aerosols in the compressed air line. Since the level of the Dry Ice trap was not maintained constant, it is likely that the temperature and humidity varied considerably. Therefore, this experiment was terminated and isotopic analyses were not performed.

Further experiments were conducted in a recently constructed "clean room" in an attempt to overcome the above difficulties.

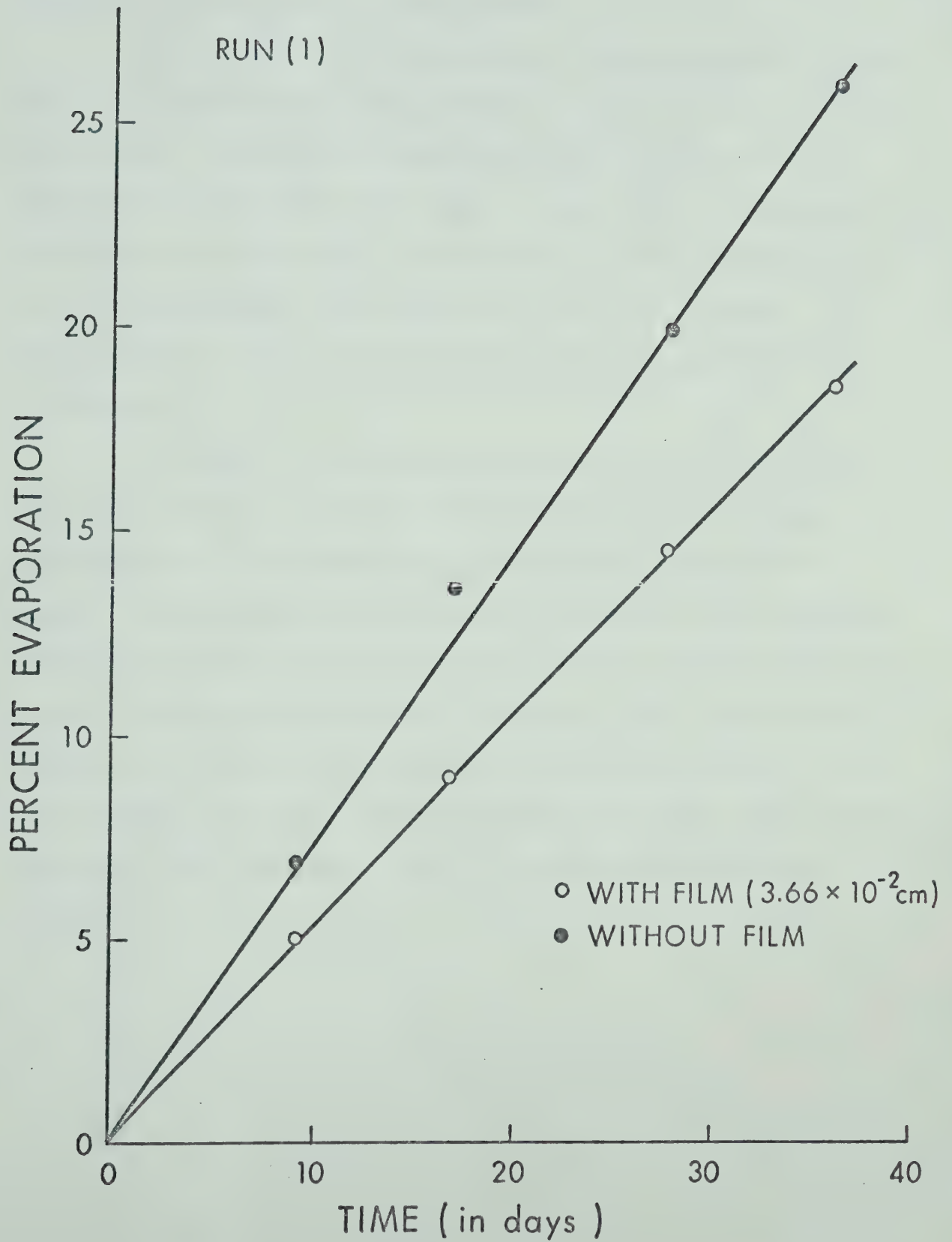


Figure 1
Percentage evaporation as a function of time

Run No. 2 (Fume hood in clean room).

Fig. 2 shows the percentage evaporation as a function of time without film and with a film of 2.44×10^{-2} cm thickness. The relative humidity was initially 20% and decreased to 17% after 46 hours. Thereafter it remained reasonably constant for the duration of the experiment. In this experiment, the effect of the film is quite pronounced in that it reduced the rate of evaporation by a factor of 4.2.

In Fig. 3, the measured values of $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ for remaining water is plotted as a function of percentage evaporation. The remaining water with film appears to become enriched in the heavier H_2O^{18} species at a slightly faster rate than that without film. The isotopic compositions of the "instantaneous" vapour and the "accumulated" vapour have been calculated from the observed values. It is seen that the H_2O^{16} species evaporates about 2.4% faster than the H_2O^{18} species. This is further discussed in Chapter 5.

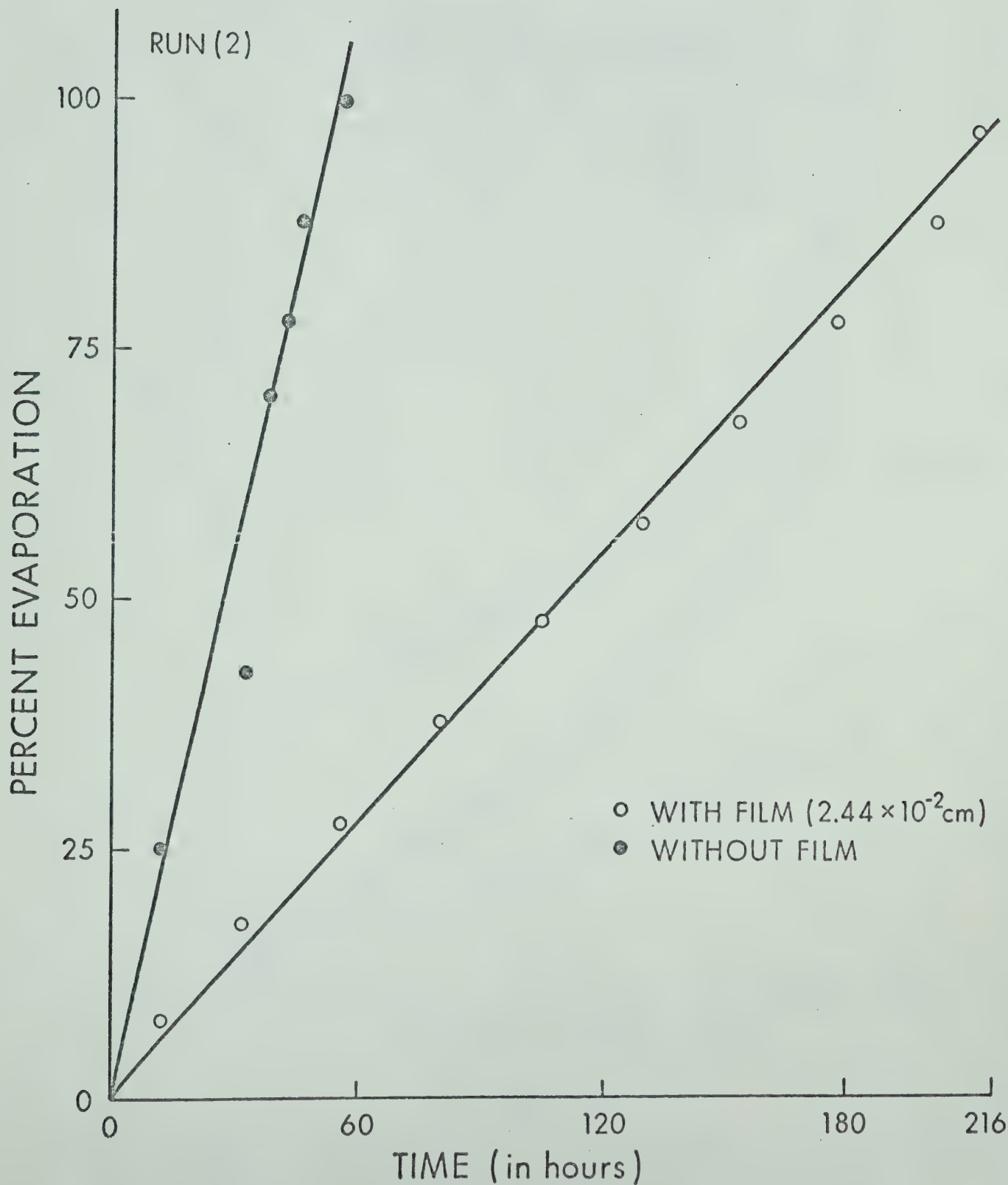


Figure 2

Percentage evaporation as a function of time

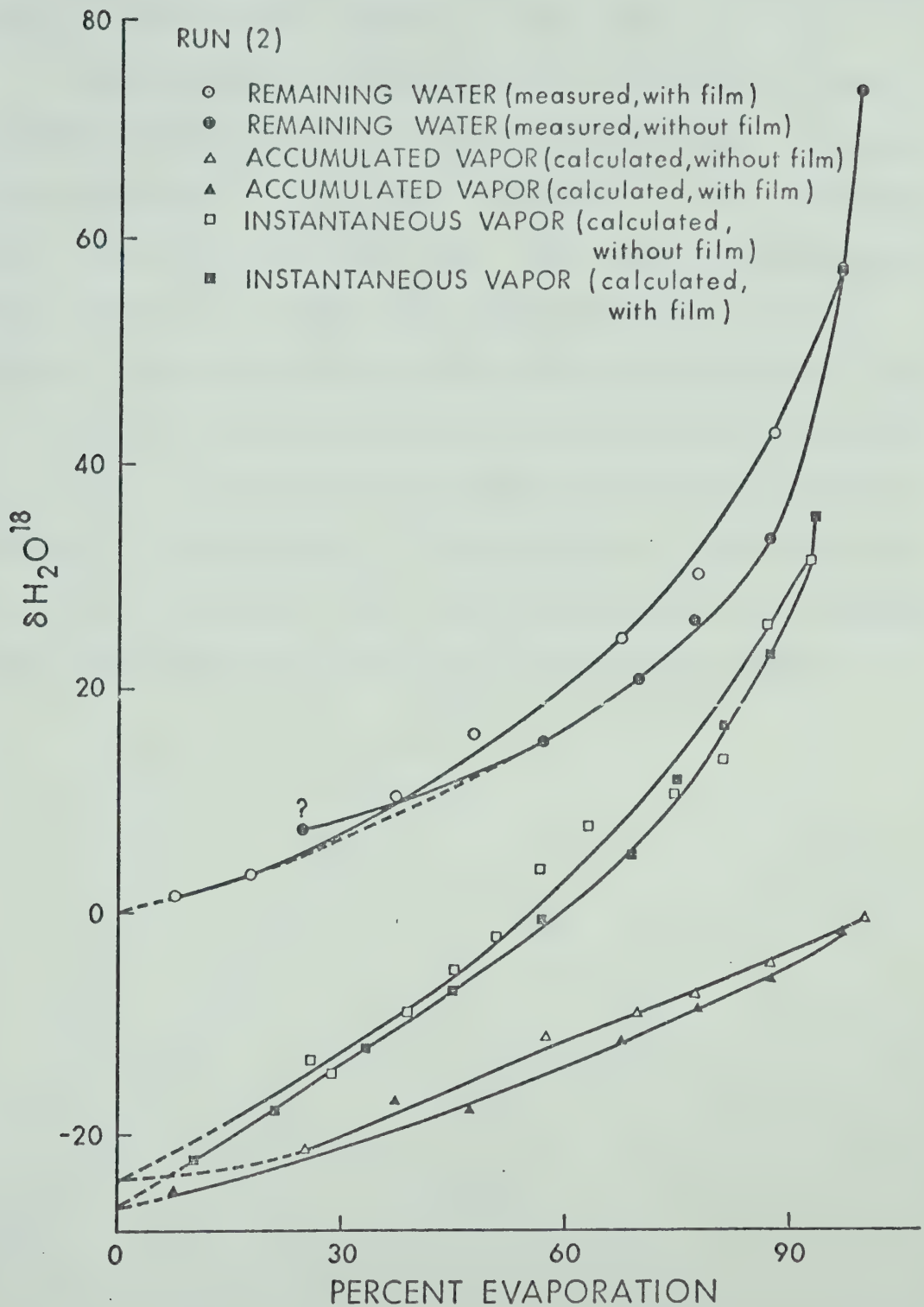


Figure 3

δH_2O^{18} of remaining water, instantaneous and accumulated vapours as a function of percentage evaporation

Run No. 3 (Clean room, outside of fume hood).

The percentage evaporation as a function of time is plotted in Fig. 4. The relative humidity was initially 20% and decreased to 17% after 68 hours. It then remained constant till the end of the run. The rate of evaporation without film was 2.2 times that with film (1.1×10^{-2} cm thickness). On the basis of the isotope data derived from Run No. 2 where the effect of the film was more pronounced than in this run, a significant difference in the isotopic behaviours is not expected. Since Run No. 6 was conducted under similar conditions with three different film thicknesses, isotopic determinations were not conducted for Run No. 3.

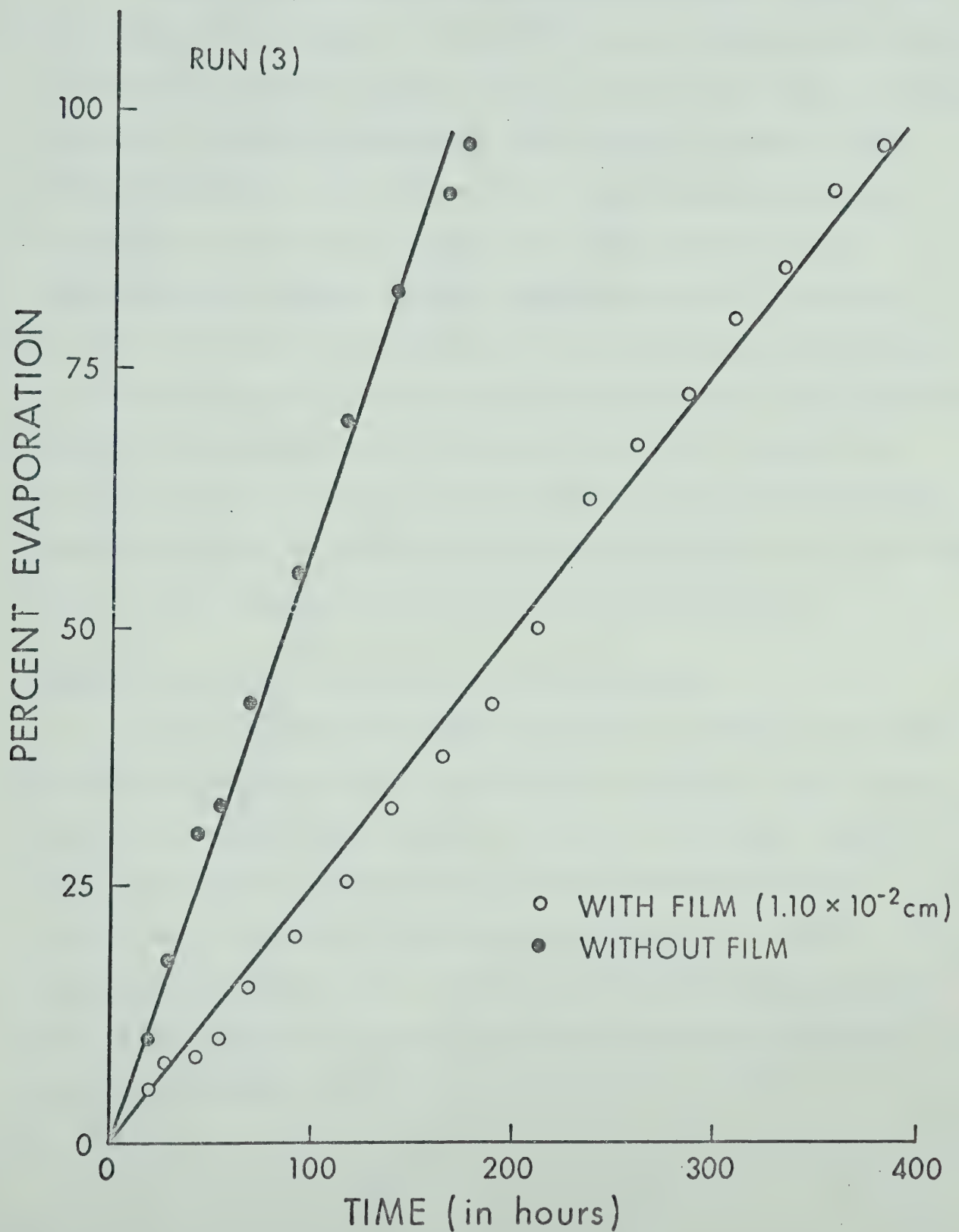


Figure 4

Percentage evaporation as a function of time

Run No. 4 (Clean room, outside of fume hood).

Fig. 5 shows the percentage evaporation without and with film of thickness 6.0×10^{-3} cm as a function of time. We observe a sudden decrease in the evaporation rate at about 100 hours. This was caused by the abrupt increase in the relative humidity from 17% to 40%. The relative humidity decreased to about 20% at about 240 hours and we note a corresponding increase in the evaporation rate. However, by this time, the water without film had already evaporated. It is noted that the rate of evaporation at the lower humidity compares favourably with the data of Run No. 3 where the average humidity was about 18%. However, since the humidity conditions were not consistent between the case with film and that without film, isotopic data were not obtained.

Run No. 5 (Clean room, outside of fume hood).

This run was not completed since a furnace was intermittently operated in the clean room at various time during the run. Although the maximum change in the water temperature was 3°C , the fluctuations in air temperature were considerably greater. For this reason, Run No. 6 was a repetition of Run No. 5. In Fig. 6, the percentage evaporation as a function of time is plotted for comparison with data from Run No. 6.

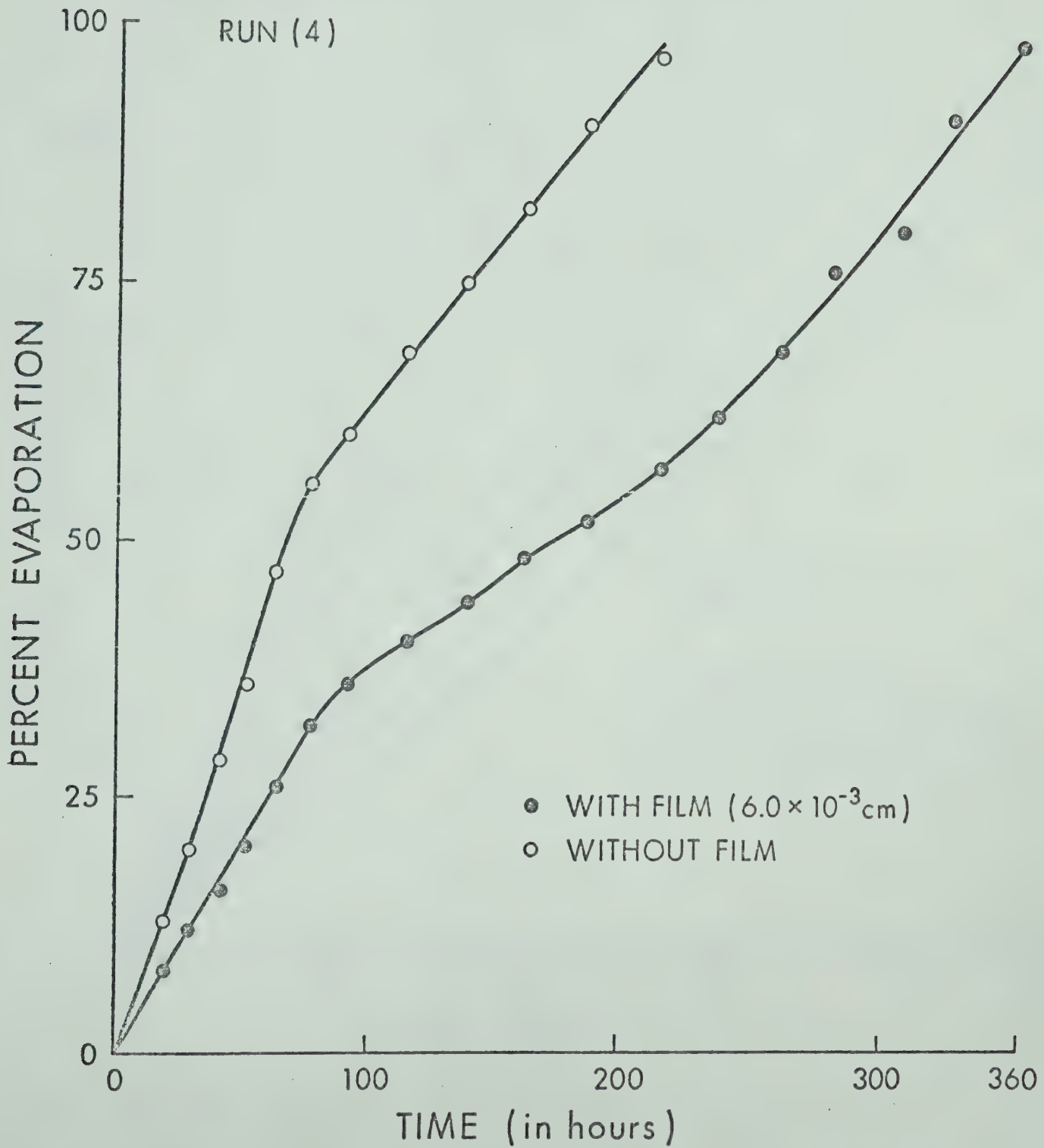


Figure 5
Percentage evaporation as a function of time

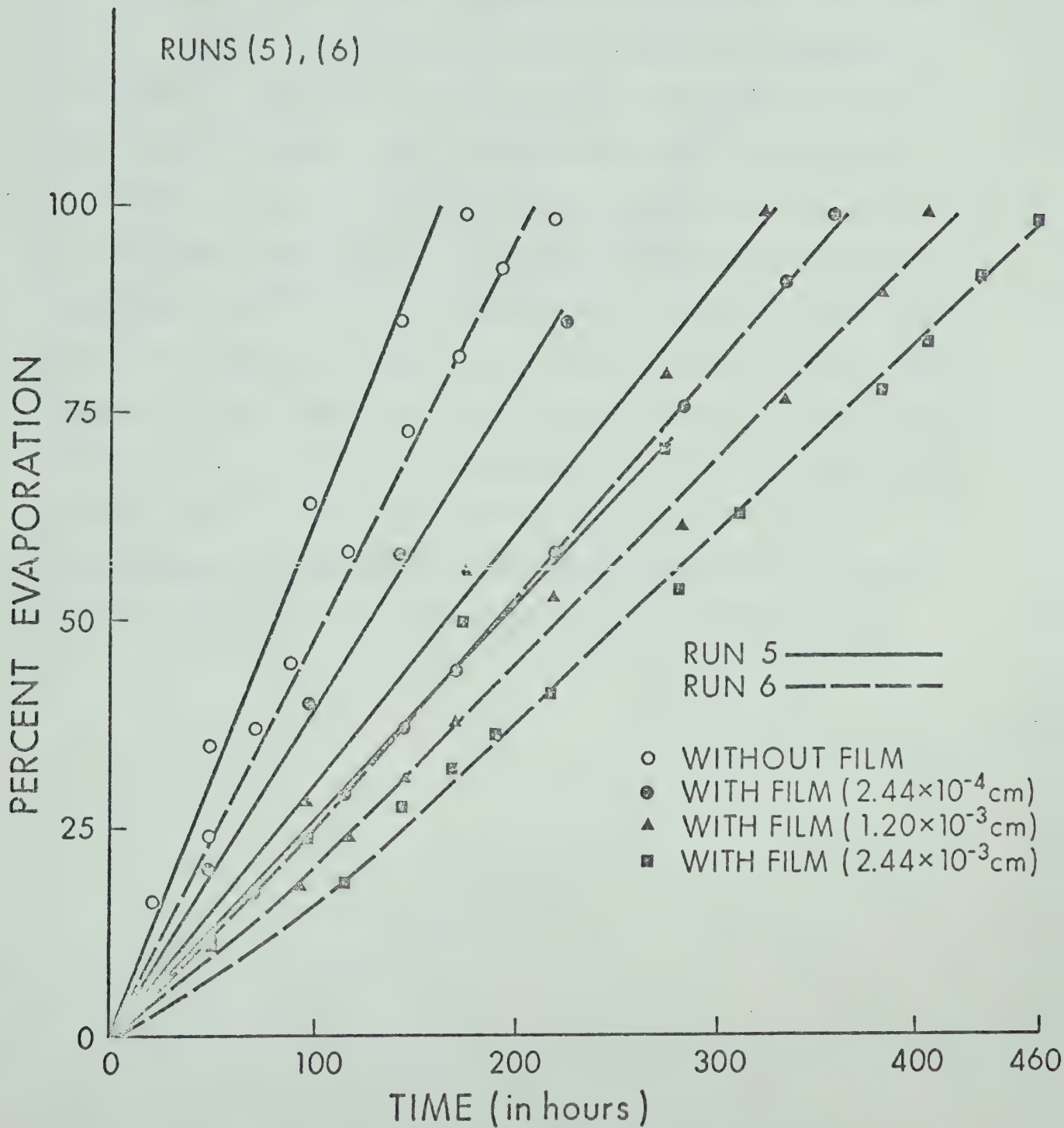


Figure 6
Percentage evaporation as a function of time

Run No. 6 (Clean room, outside of fume hood).

Fig. 6 shows the percentage evaporation as a function of time without film and with films of thicknesses 2.44×10^{-4} , 1.20×10^{-3} and 2.44×10^{-3} cm respectively. Here, as in Run No. 2 we observe that H_2O^{18} content of the remaining water without film is slightly lower than in the cases with films. Although the data are not overwhelmingly convincing, it appears that as the thickness of the film increases, there is a slight increase in the H_2O^{18} content of the remaining water (Fig. 7). The theoretical lines in Fig. 7 will be discussed in Chapter 5. The calculated $\delta\text{H}_2\text{O}^{18}$ values for the "instantaneous" and the "accumulated" vapours in each case are plotted in Figs. 8 to 11. These data will also be discussed in Chapter 5.

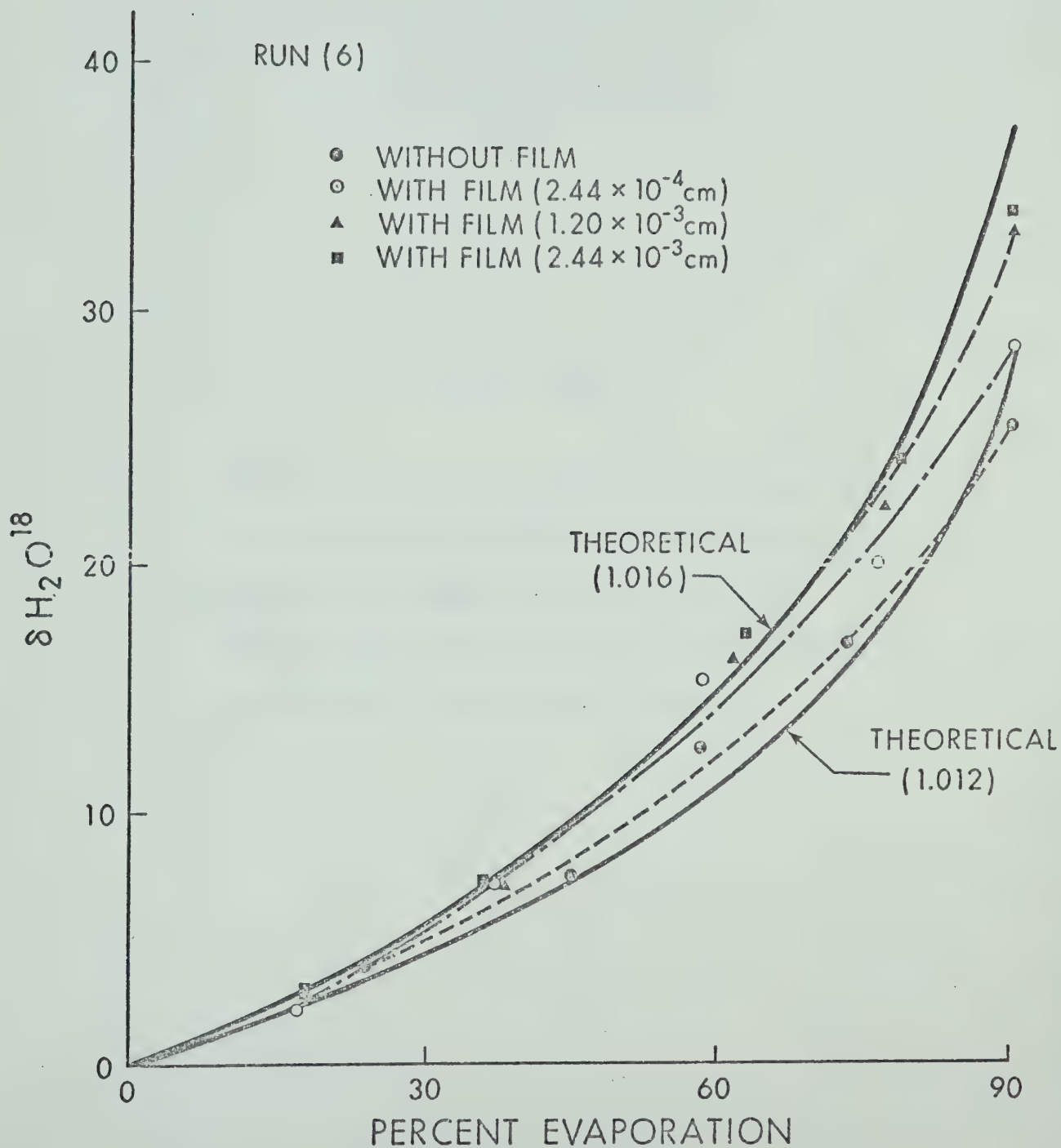


Figure 7

δH_2O^{18} of remaining water as a function of percentage evaporation compared to theoretical values derived from REES' program

Figures 8-11

$\delta\text{H}_2\text{O}^{18}$ of remaining water, instantaneous and accumulated vapours as a function of percentage evaporation for the cases without film and with films of 3 different thicknesses respectively (Run 6)

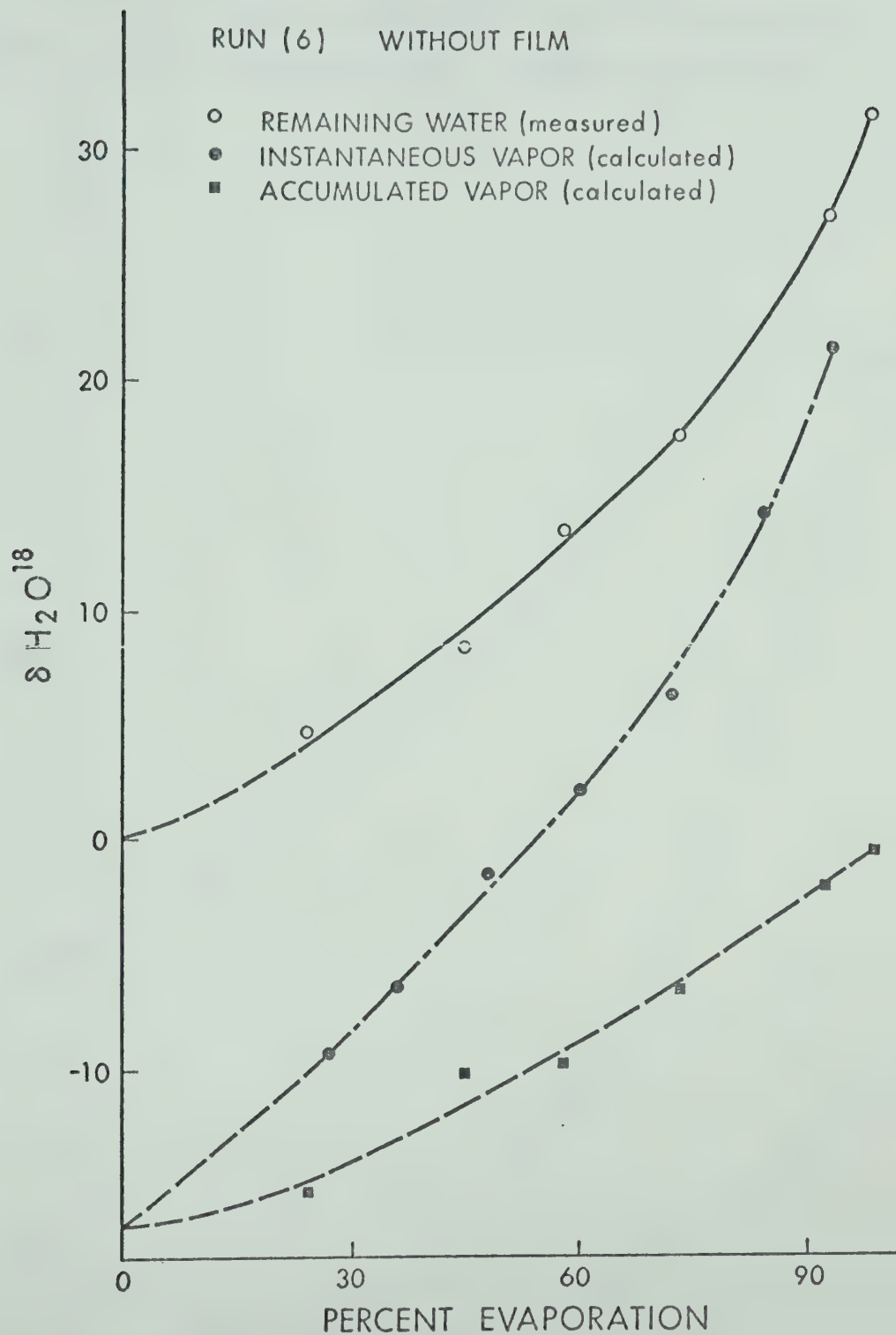


Figure 8

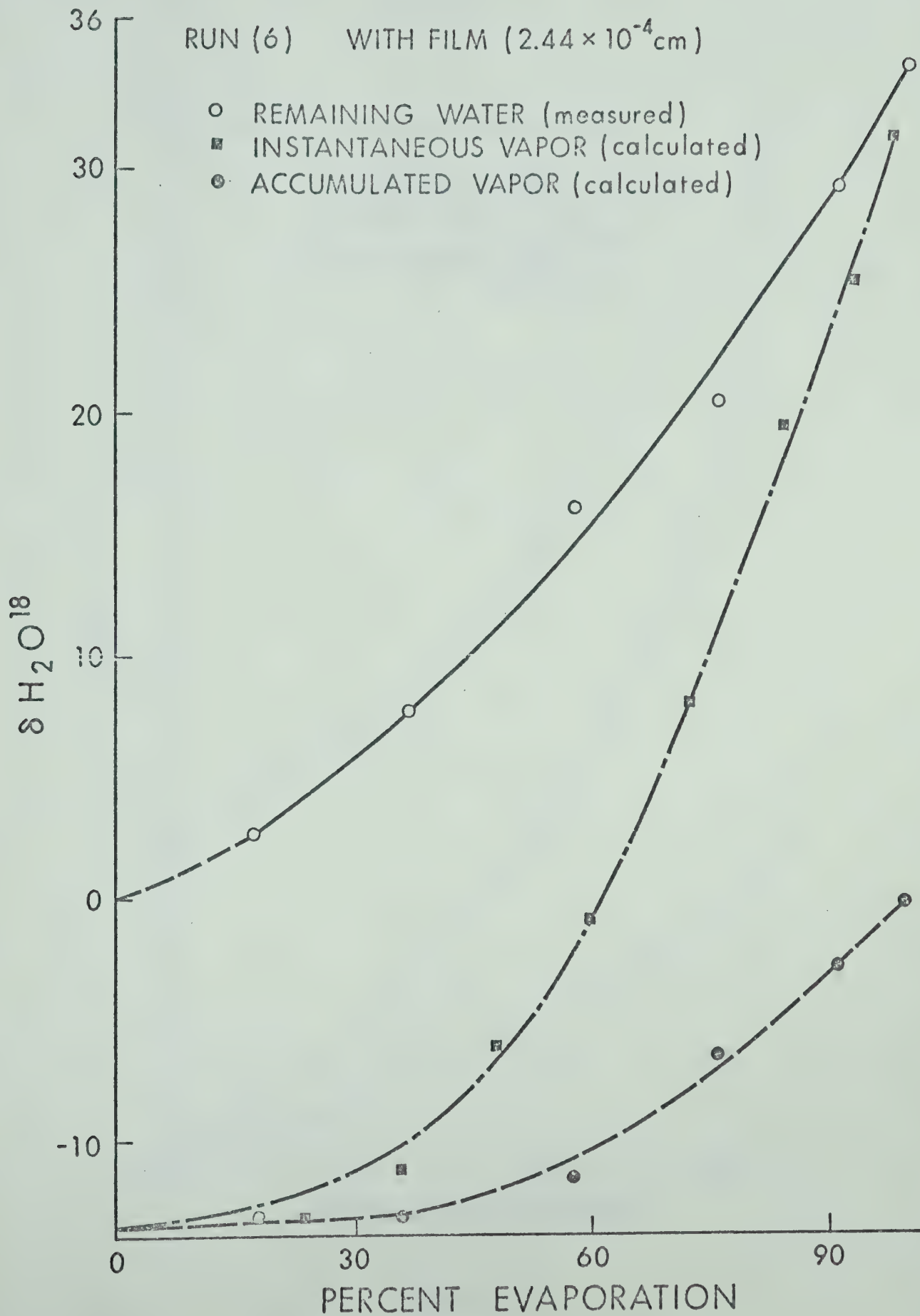


Figure 9

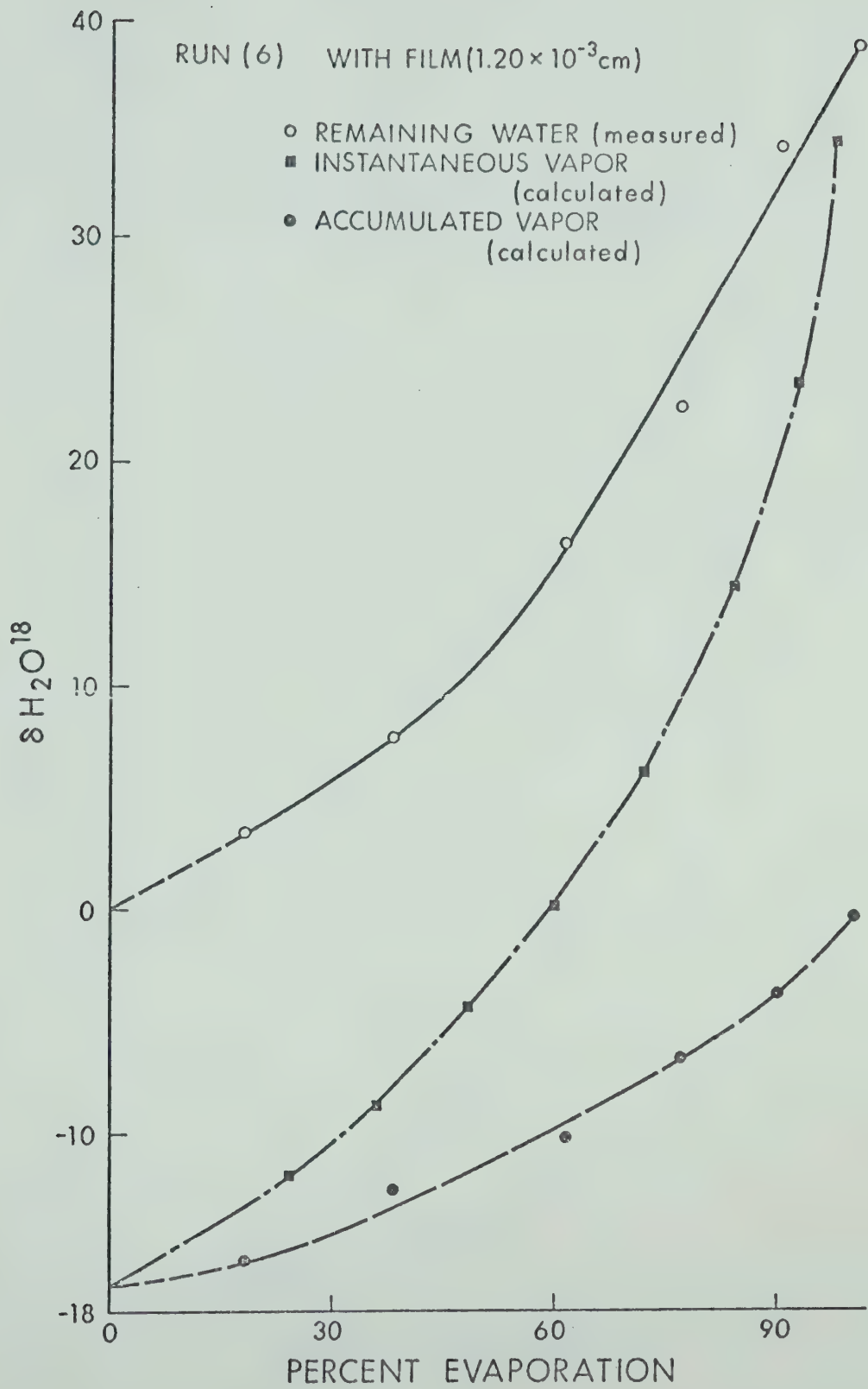


Figure 10

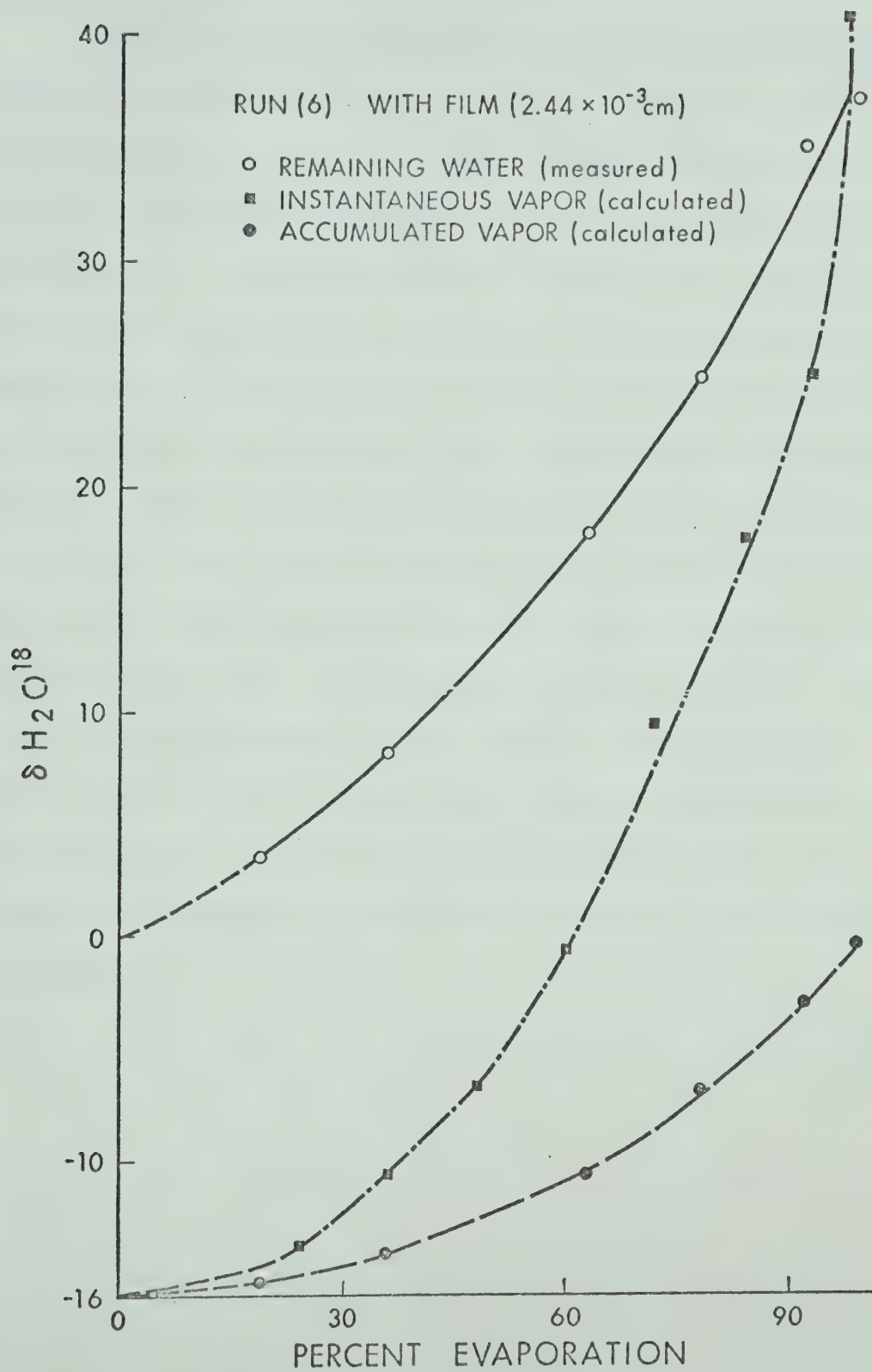


Figure 11

Run No. 7 (Clean room, under fume hood).

The percentage evaporation as a function of time without film and with films 4.88×10^{-4} and 2.44×10^{-3} cm thick is shown in Fig. 12. The relative humidity was initially about 45% and started to increase gradually till it reached 70% after 200 hours. However, the rate of evaporation was not altered very much. This experiment was carried out in the presence of other activity in the fume hood, which may have caused such a sharp rise in the relative humidity. After 125 hours the water without film evaporated. We note that the rate of evaporation in this run reasonably compares with the data of Run No. 2 which was also conducted under the fume hood. However, the observed δH_2O^{18} values of the remaining water in this run is almost half of those obtained in Run No. 2 (Fig. 13). Figs. 14 to 16 show the calculated δH_2O^{18} values for the "instantaneous" and the "accumulated" vapours in each case which will be discussed in Chapter 5.

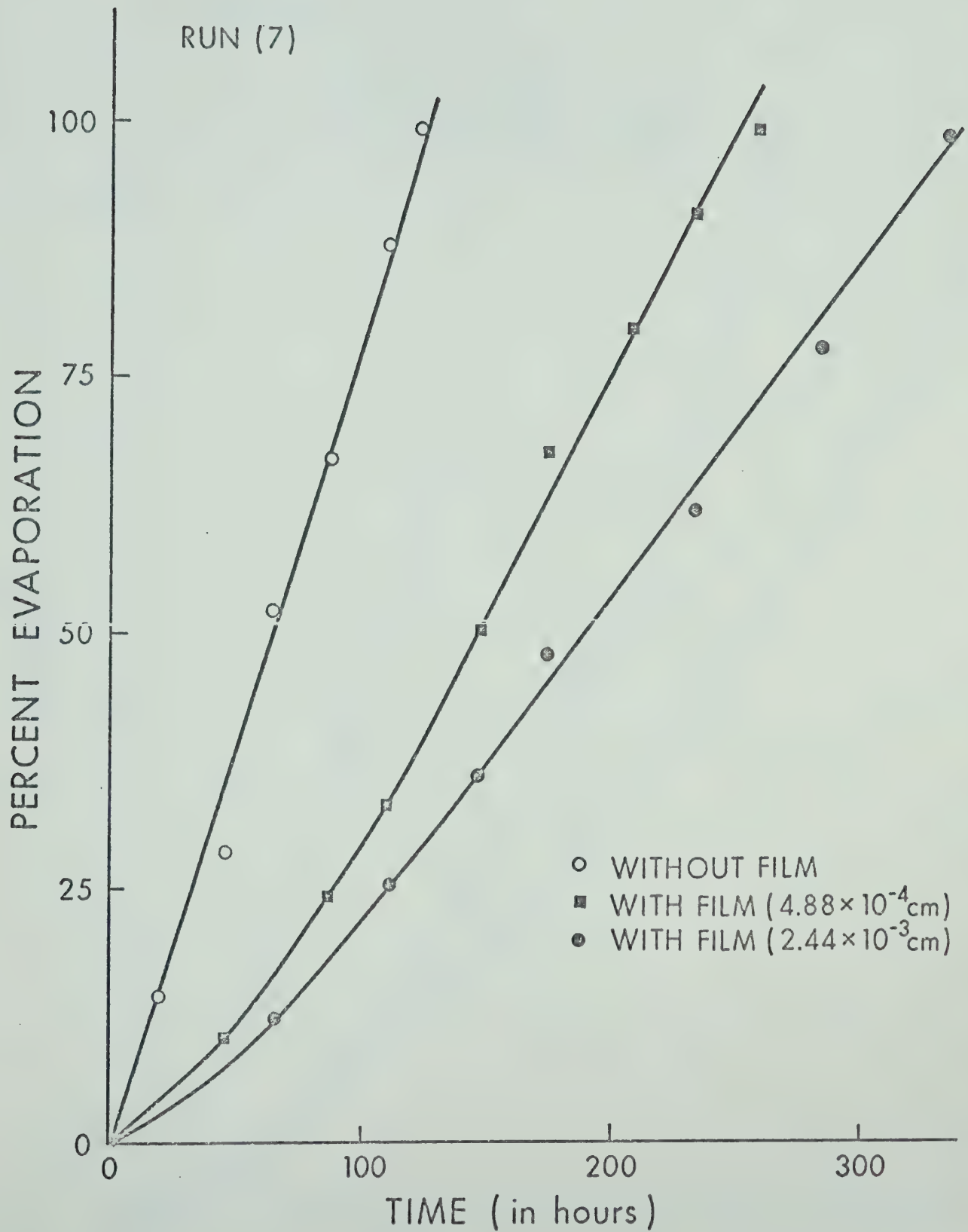


Figure 12
Percentage evaporation as a function of time

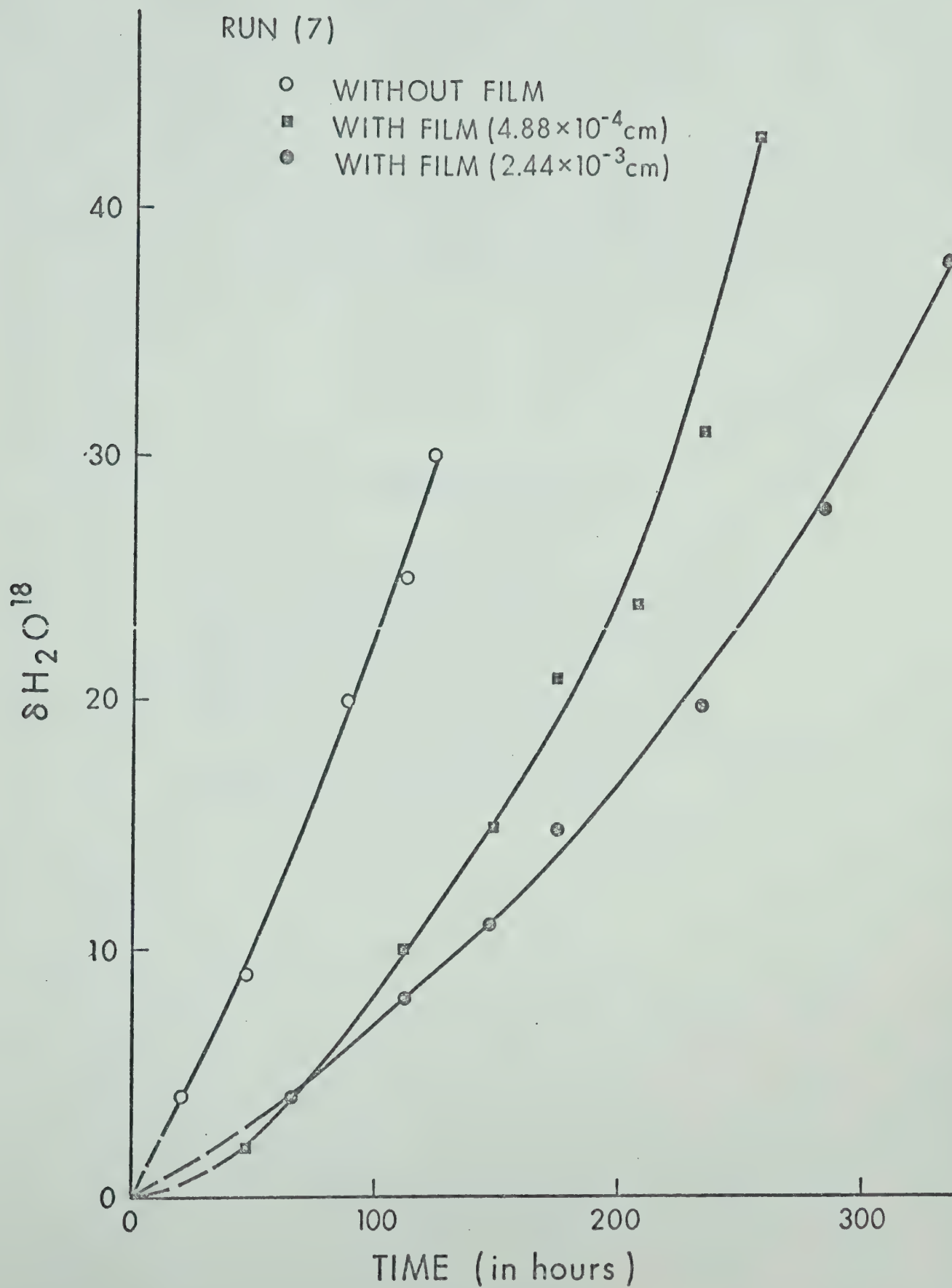


Figure 13
 δH_2O^{18} of remaining water without film and with

Figures 14-16

$\delta\text{H}_2\text{O}^{18}$ of remaining water, instantaneous and accumulated vapours as a function of percentage evaporation for the cases without film and with films of 2 different thicknesses respectively (Run 7).

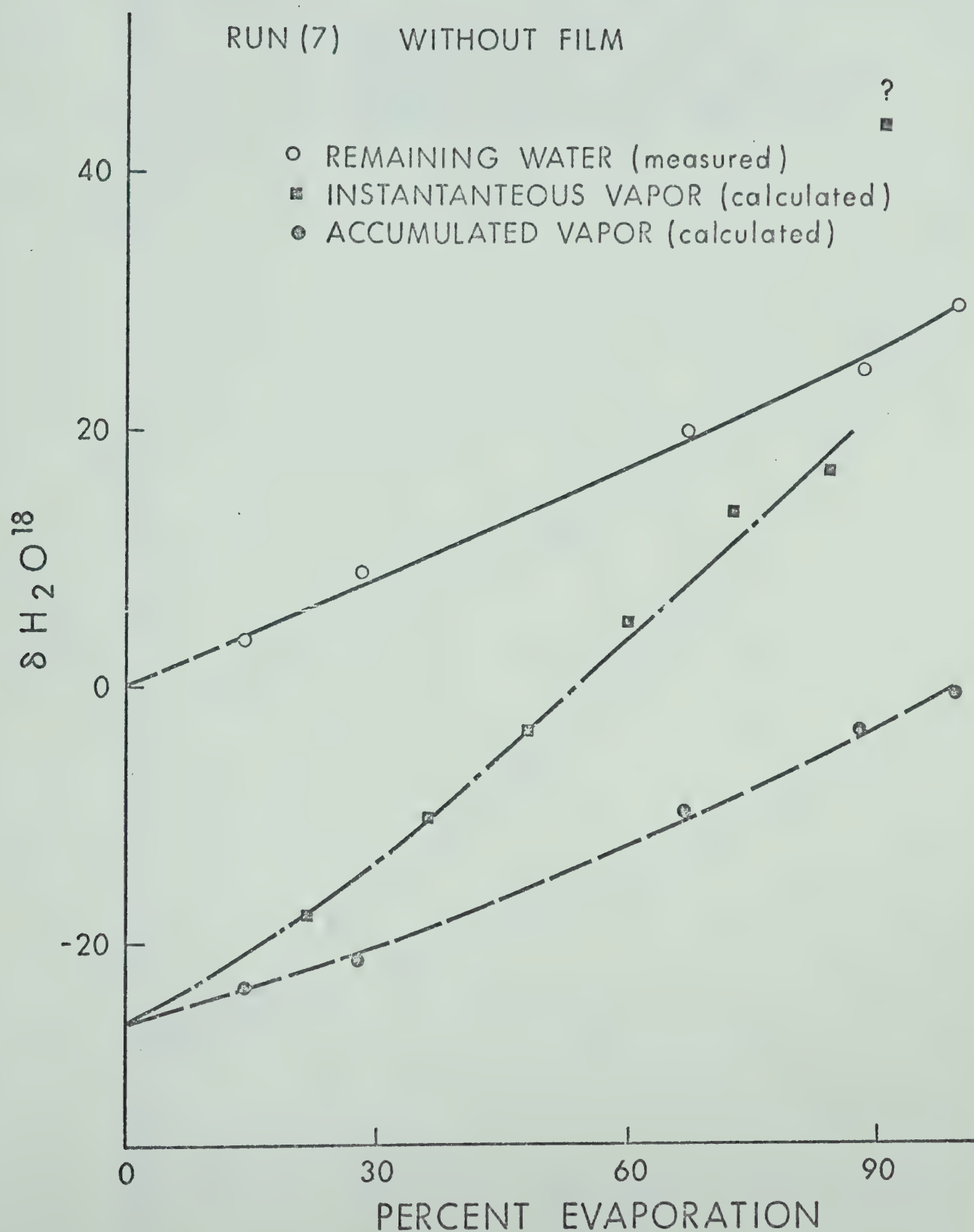


Figure 14

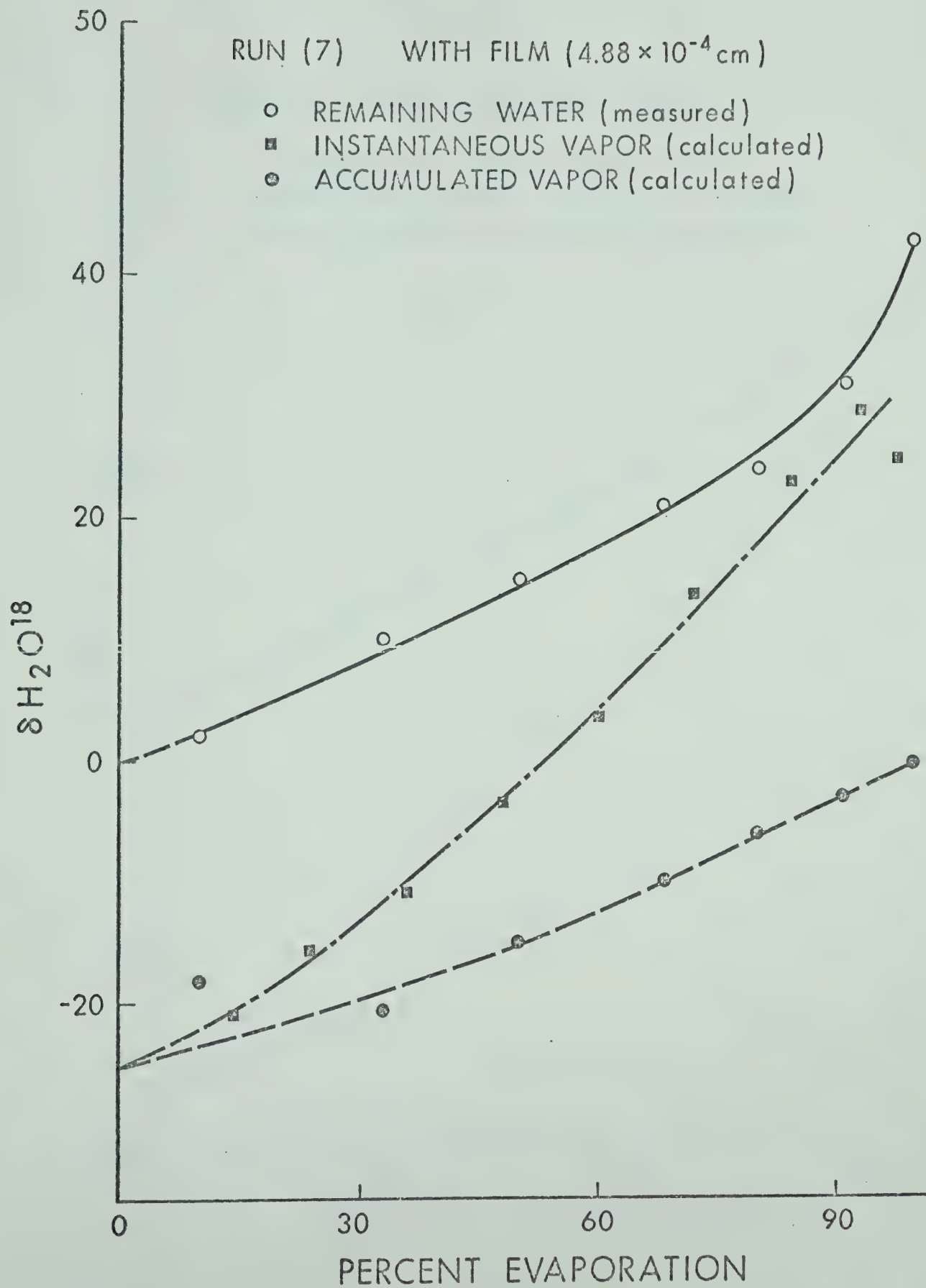


Figure 15

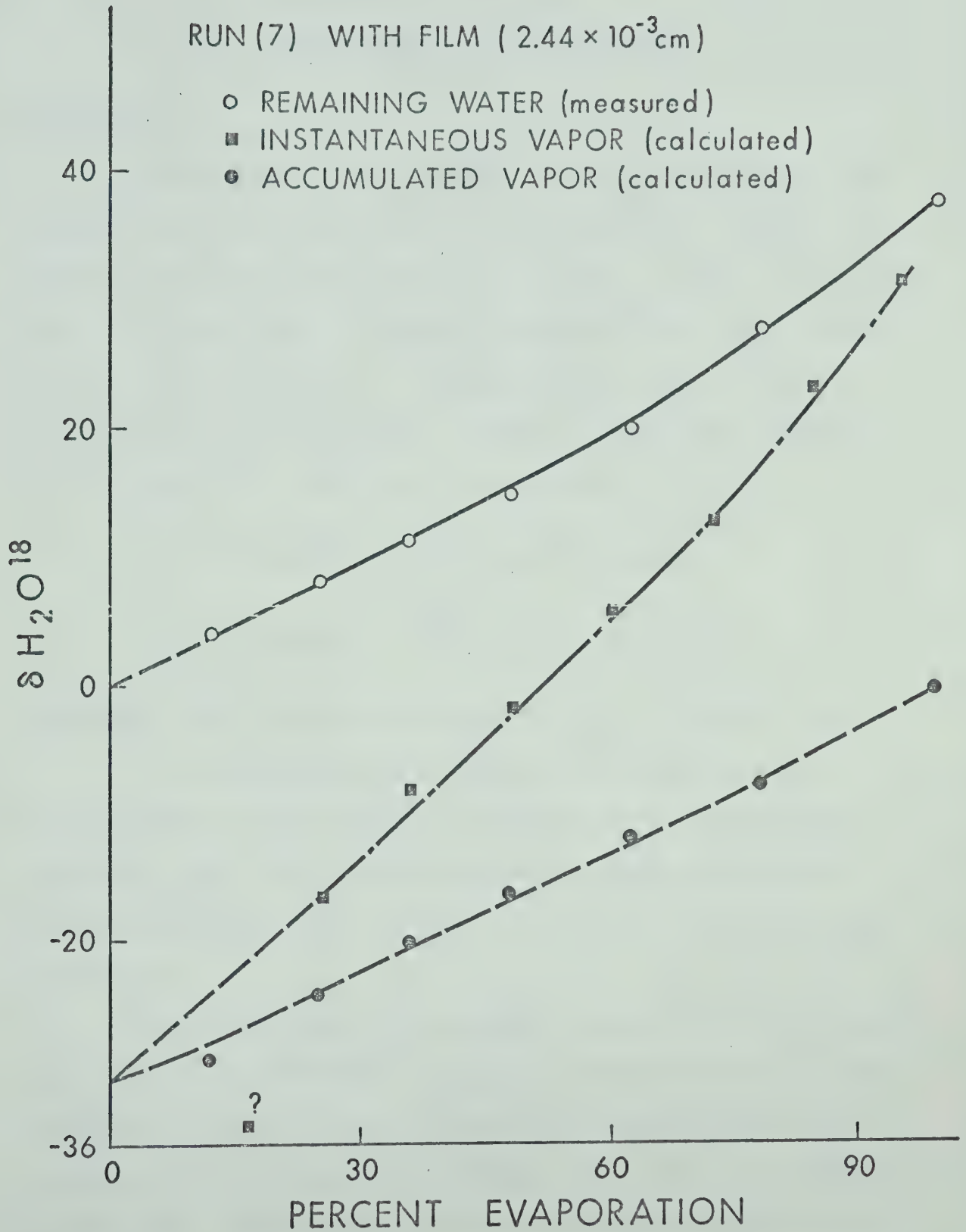


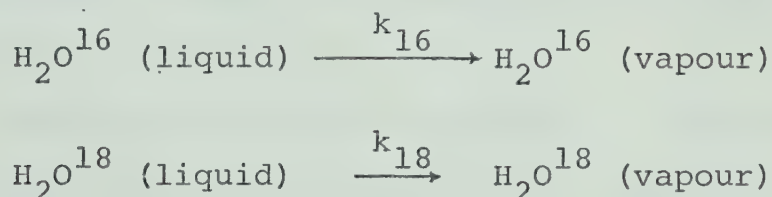
Figure 16

CHAPTER 5

DISCUSSION AND CONCLUSIONS

DISCUSSION

H₂O vapour in equilibrium with H₂O liquid at room temperature should be about 9 ‰ depleted in δH₂O¹⁸ as compared to the liquid (DANSGAARD, 1964). Since the isotopic fractionations of these experiments are much larger, it would seem that we are dealing mainly with a non-equilibrium situation which can be described most simply by the competitive isotopic evaporations



DANSGAARD (1961) measured values of k_{16}/k_{18} up to 1.019.

The evaporation rate should be proportional to surface area in the absence of significant surface motion. Therefore, the rate of evaporation in any one container should remain the same. Figures 1 to 6 and 12 verify this contention.

In considering the isotopic selectivity, in evaporation, it seems reasonable to include all available liquid molecules since the surface molecules should effectively exchange with the deeper molecules. Thus, for any isotopic species, the evaporation rate should be proportional to the number of that species available in the liquid state. This

is analogous to first order reactions in chemistry where the reaction rate depends on concentration of a reactant to the first power. Equations for first order competing isotopic reactions have been derived by many authors (BIGELEISEN, 1949; HARRISON and THODE, 1958; NAKAI and JENSEN, 1964). REES (1964) has used computer programming to evaluate the parameters "isotopic composition of remaining reactant" and "isotopic composition of accumulated product" for different ratios of isotopic rate constants. The values listed in Table 1 in Chapter 2 which were taken from DANSGAARD (1964) are consistent with those given in this computer program.

REES' program was used in Fig. 7 (Run No. 6) to draw theoretical lines based on $k_{16}/k_{18} = 1.012$ and 1.016 for the isotopic behaviour of the remaining water. It is seen that most points in this run fall within these limits. This run was conducted outside the fume hood in the clean room.

This program was then used to derive k_{16}/k_{18} ratios from measured values of δH_2O^{18} of the remaining water at various percentages of evaporation. Note that these derivations give average values of k_{16}/k_{18} up to the percentages of evaporation being considered. These data are summarized in Table 2. It is seen that $\overline{k_{16}/k_{18}}$ fluctuates considerably in the runs. This implies even greater fluctuations in instantaneous values of k_{16}/k_{18} . In particular, it is seen that Run No. 7 which was conducted under the fume hood departs markedly from this first order behaviour.

Table 2

Values of $\overline{k_{16}/k_{18}}$ at different times and
evaporations, obtained from REES' program

<u>Run No.</u>	<u>Film thickness (cm)</u>	<u>Time (hours)</u>	<u>Percent evaporation</u>	<u>δH_2O^{18} of remaining water (mea- sured, ‰)</u>	<u>k_{16}/k_{18}</u>
2	nil	12	25	7.47	1.026
		32.5	57.5	15.14	1.018
		38	70	20.78	1.017
		42	77.5	26.05	1.016
		46	87.5	32.99	1.016
2	2.44×10^{-2}	12	7.5	1.74	1.022
		32.5	17.5	3.47	1.018
		81	37.5	10.36	1.022
		105	47.5	15.69	1.024
		129	57.5	19.61	1.023
		153	67.5	24.28	1.021
		177	77.5	29.81	1.020
		201	87.5	42.40	1.020
		211.5	96.8	56.92	1.015
6	nil	48	24	4.75	1.017
		89	45	8.29	1.014
		116	58	13.40	1.015
		144	73	17.52	1.013
		190	92.5	27.01	1.011
		217.5	98.5	31.41	1.008
6	2.44×10^{-4}	71	17	2.66	1.014
		144	37	7.81	1.019
		281	76	20.78	1.014
		331	91	29.46	1.012
		354	99.4	34.47	1.0075

Table 2 (cont'd)

Run No.	Film thickness (cm)	Time (hours)	Percent evaporation	$\delta\text{H}_2\text{O}^{18}$ of remaining water (measured, ‰)	k_{16}/k_{18}
6	1.2×10^{-3}	92	18	3.53	1.018
		169	38	7.77	1.016
		281	61.5	16.34	1.0175
		331	77	22.52	1.0155
		379	90	33.99	1.0145
		402.5	99.9	38.69	1.0085
6	2.44×10^{-3}	116	18.5	3.55	1.0175
		190	36	8.02	1.018
		310.5	63	18.0	1.018
		379	78	24.93	1.0165
		429	92	35.05	1.0135
		438	99	37.22	1.008
7	nil	20	14.5	3.95	1.0235
		46	28.5	8.69	1.0255
		66	52	-	-
		87.5	67	20.33	1.0185
		111.5	88	25.33	1.0115
		124	99.4	30.06	1.0065
7	4.88×10^{-4}	46	10	2.00	1.0215
		111.5	33	9.86	1.024
		147.5	50	15.21	1.022
		175	68	21.42	1.0185
		208	80	23.94	1.0145
		234	91	30.54	1.0125
7	2.44×10^{-3}	257	99.6	43.17	1.0095
		66	12	3.56	1.0275
		111.5	25	7.82	1.027
		147.5	36	10.87	1.0245
		175	48	15.10	1.023
		234	62	19.93	1.0205
7	2.44×10^{-3}	284	78	27.69	1.018
		335	98.8	37.87	1.0095

The values of δD for all the samples of Run No. 6 were measured by BUCKLEY (1971). Within rather large errors due to instrumental problems, the isotopic fractionation without film and with films of different thicknesses are the same.

The difficulties in interpreting these experiments arise mainly because it was impossible to maintain constant conditions throughout any one set of experiments. This is shown clearly in Fig. 5 where the evaporation rate decreased markedly with an increase in humidity.

It would seem that one might overcome these difficulties by ascertaining k_{16}/k_{18} for all containers in the series at any one time. However, Fig. 17 shows that $\overline{k_{16}/k_{18}}$ is not consistent in all the containers at any one time. For some reason, it generally decreases towards the end of each individual evaporation. When $\overline{k_{16}/k_{18}}$ is plotted as a function of percentage evaporation, we find that the curves in any one run are more consistent (Fig. 18). Thus it seems that conditions change in any one container as evaporation proceeds. Since the depth of the containers was comparable to the other dimensions, it would seem that "edge effects" are responsible for the observed behaviour.

It is seen in Fig. 18 that Run No. 6 which was out in the open in the clean room has reasonably constant k_{16}/k_{18} values up to roughly 75% evaporation whereas Run No. 7 which was in the fume hood has k_{16}/k_{18} steadily

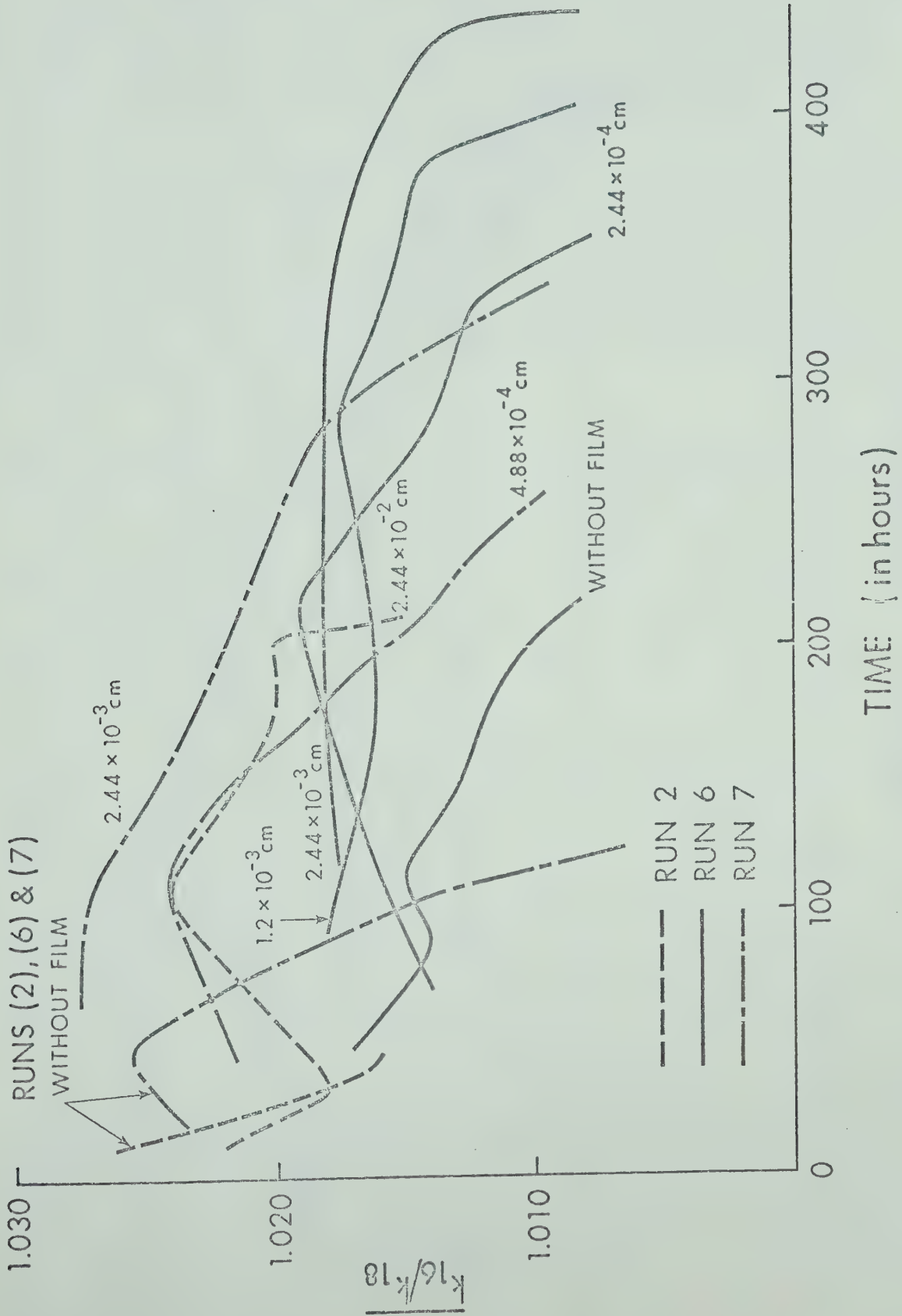


Figure 17

Average kH_2O^{16}/kH_2O^{18} as a function of time (derived from REES' program, 1964)

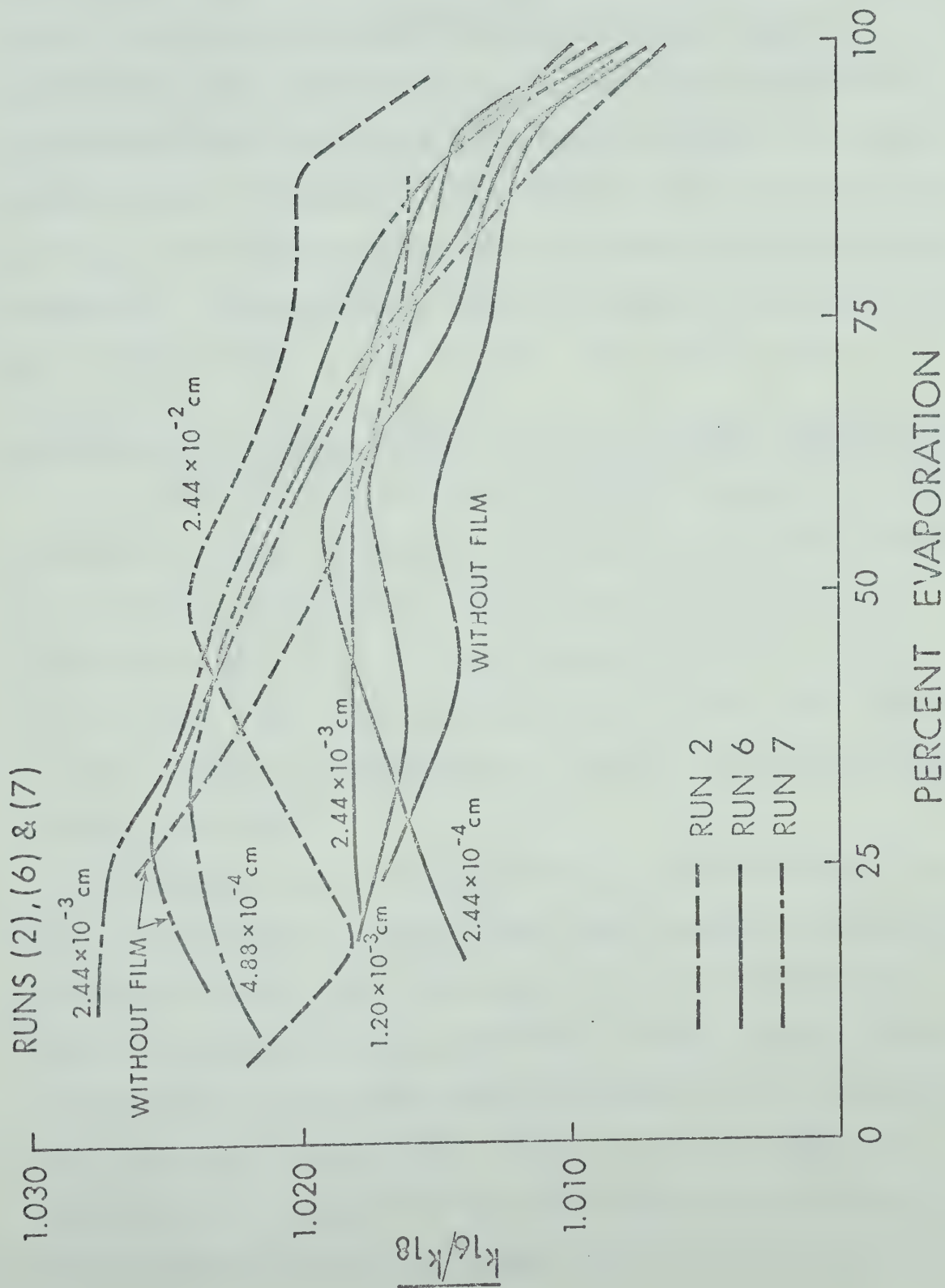


Figure 18

Average kH_2O^{16}/kH_2O^{18} as a function of percentage evaporation
(derived from REES' program, 1964)

decreasing throughout the course of the evaporation. Other than the above suggestion that container design is a related factor we are unable to explain these k_{16}/k_{18} behaviours. It is noteworthy that the literature lacks sufficient data for such a fundamental process. To elucidate the role of cetyl alcohol films in evaporation retardation, it is not necessary to fully understand this k_{16}/k_{18} behaviour. We are simply comparing isotopic behaviour with and without films.

Assessment of errors; Suggestions for improved experimentation

From the viewpoint of H_2O^{18}/H_2O^{16} analysis, errors involved in sample preparation and mass spectrometry should give δH_2O^{18} values consistent to better than ± 0.2 ‰ (standard deviation). If the storage bottle for a sample is not tight, the isotopic composition becomes more enriched in H_2O^{18} because of preferential evaporation of the lighter isotopic species.

Most of the inconsistencies in experiments of this thesis arise from the conditions under which the experiments by necessity had to be conducted. It was argued in the discussion above that one could not compare isotope fractionations at fixed times since the shape of the container must have been a significant factor. One can make the comparisons in terms of fixed percentages of evaporation IF the external conditions remain constant. However, it

was usually the case that after the water without film had evaporated the external conditions changed. Therefore, water without and with different film thicknesses did not undergo their evaporation under equivalent conditions.

It is therefore recommended that better control of these experiments would result if -

- (1) they were carried out in environmentally controlled rooms, i.e. constant temperature, humidity and air flow throughout any given run;
- (2) clean air should be involved in order to avoid the formation of additional films on the surfaces;
- (3) a container of large area and shallow depth would seem preferable in order to minimize effects at the container edges. In order to ascertain the amount evaporated continuous weighing should be a convenient technique.

CONCLUSIONS

This set of experiments, although far from ideal in many ways, have demonstrated the effectiveness of cetyl alcohol films in retarding the evaporation of water.

The isotopic measurements statistically suggest that the fractionation with films is slightly larger than without films. Further, increased film thicknesses appear to promote an increase in the isotopic selectivity during evaporation.

Much controversy in the literature has arisen in discussing the role of monolayers. We were not successful in obtaining monolayers in our experiments. However, if one extrapolates our isotopic data to smaller thicknesses, the isotopic differences between evaporation with and without monolayers should be negligible. The data of this thesis suggest that monolayers and thin films of cetyl alcohol do not introduce an isotopically dependent step which can compete effectively for rate control of the evaporation. This conclusion is further supported by the fact that the films did not alter the peculiar behaviours of k_{16}/k_{18} as a function of percentage evaporation (Fig. 18). In other words, placing the containers in a fume hood or in the open altered the isotopic behaviour to a greater extent than varying the film thickness. The data may support the conclusion that the role of films is simply that of decoupling air currents from the water surface as proposed by MacRITCHIE (1969). It would seem however that there were definite "edge effects" in the containers used. If the films actually decoupled air currents from the water surface, they should have reduced such edge effects.

Thus, the addition of films to water surfaces does not offer advantages for commercial isotopic separation purposes. If thicker films or other materials promoted larger isotopic selectivity, one still has the problem that the covered surfaces require longer times for evaporation.

It would also seem that fractionation of isotopic species of water in the hydrologic cycle is not influenced much by the presence of surface films.

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